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Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air

ATC, Inc., Auburn, AL

Prepared for:

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The guidance document was originally issued in June 1983. Since then significant changes have occurred in the regulations that cover volatile and semivolatile organic air pollutants. There have also been significant advances in the collection and analysis of organic compounds and in the quality and availability of calibration and QC samples for them. This present version of the guidance document has been revised to reflect these changes so that this new information can be readily available to the monitoring community. Because the document covers regulatory issues, sampling and analytical methods, monitoring plan development and quality assurance it will be useful to both governmental and industrial personnel concerned with monitoring the ambient air for organic compounds. It should be useful as an aid for planning and establishing such air monitoring programs, but it should not be used as the sole source for such a program.

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by

ATC, Inc.
1635 Pumphrey Ave.
Auburn, Alabama 36830

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EPA Project Officer:

Howard Crist
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

This Technical Assistance Document (TAD) was initially published in June 1983 and has been updated to reflect the advances that have been made in sampling and analysis of toxic organic compounds in ambient air. The primary users of this document are expected to be regional, state, and local environmental protection personnel who are faced with the need to determine ambient air quality for regulatory or information-gathering purposes.

The TAD consists of the following seven chapters:

1. Introduction
2. Regulatory Issues Concerning Toxic Organic Monitoring
3. Guidelines for Development of a Monitoring Plan
4. Overview of Sampling Methods
5. Overview of Analytical Methods
6. Methods for Specific Compounds and Compound Classes
7. Quality Assurance

PREFACE

The determination of toxic organic chemicals in ambient air is an area of concern for many environmental protection personnel. There exist intense regulatory pressures to gather data concerning human exposure to such chemicals. During the last five years, sampling and analysis methods for toxic organic air pollutants have become increasingly standardized, and standard reference materials for the compounds have become available. This technical assistance document (TAD) has been revised for the purpose of providing such personnel with a basis for developing specific monitoring plans for toxic organic chemicals, in light of the advances that have been made in these areas; however, this document does not circumvent the need to have highly skilled technical personnel organizing such monitoring efforts, and the TAD should not be used as a rigid, step-by-step guide for developing monitoring plans.

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SECTION 1

INTRODUCTION

The Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air was initially published in June of 1983 and was intended as a guide to those persons responsible for designing and implementing ambient air monitoring programs for toxic organic compounds. Since that date, there have been significant advances in methodology for analyzing toxic organic air pollutants (TOAP's), significant improvements in the quality and availability of calibration standards for TOAP's, and significant changes in TOAP regulations. The combined impact of these factors limited the vitality of the TAD and necessitated revision of the original document to reflect advances in the field.

This Technical Assistance Document (TAD) is intended for use by regional, state, and local environmental regulatory personnel. It may also be useful to the regulated community in terms of the development of TOAP monitoring programs. The TAD is not intended to serve as a single source of information from which all necessary technical input concerning TOAP monitoring can be obtained. Instead, it is a guidance document which can be used as a basis for the development of TOAP monitoring programs.

The revised TAD is presented in seven major sections, including this introductory section. Section 2 provides fundamental information concerning risk assessment and addresses the regulatory issues which result in a need for TOAP monitoring programs.

Section 3 focuses on the factors which impact the development of a TOAP monitoring program. The emphasis of this section is adequate TOAP monitoring program planning to achieve established objectives. Topics addressed include program design based on data quality objectives, evaluation of available information, selection of sampling and analytical protocols, specification of quality assurance protocols, data reporting, safety considerations, and manpower requirements. The information is presented in a manner which implies step-wise progression through the planning process; however, actual TOAP monitoring program planning is an iterative process wherein conflicts between program objectives and limitations of the various planning elements are reconciled.

Section 4 provides an overview of sampling methods for TOAP's. Sampling methodologies are reviewed on the basis of chemical and physical properties. Most of this section is dedicated to procedures for volatile and nonvolatile TOAP's. Advances in sampling protocols for phase distribution analysis of semi-volatile TOAP's are also reviewed in this section.

Section 5 provides an overview of the various analytical protocols for TOAP's. Field screening and laboratory screening techniques are discussed in general terms. This section concludes with a discussion of compound specific analytical techniques.

Section 6 serves to integrate the basic information contained in Sections 4 and 5 and addresses sampling and analytical approaches for specific organic compounds. The highlight of Section 6 is a table summarizing sampling and analytical protocols suitable for several of the organic compounds subject to regulation under Section 112 of the Clean Air Act.

Section 7 provides information concerning the various components of an effective quality assurance program for a TOAP monitoring program. The emphasis of this section is on system design, document control, data storage, quality audits, reports, training, equipment calibration, equipment maintenance, calibration, reference materials, and method validation.

SECTION 2

REGULATORY AND RELATED ISSUES CONCERNING TOXIC ORGANIC MATERIALS

2.1. GENERAL

The primary motivations for conducting ambient air monitoring of TOAP's are: (a) regulatory compliance requirements, (b) emergency situations (chemical spills, inadvertent releases, and fires) and nuisance complaints, and (c) air pollution research activities. Each of these topical areas has distinct requirements for ambient air monitoring which are important to recognize. While each area may have distinct requirements, the impetus for TOAP monitoring programs is the risk to human health associated with exposure to TOAP's.

2.2. RISK ASSESSMENT

Toxic Organic Air Pollutants are the focus of regulatory concern because of the adverse health effects associated with their uncontrolled presence in the environment. The establishment of ambient air quality standards for TOAP's is difficult because of the variety of compounds of concern, the economics of TOAP control, and the inherent problems associated with documenting the rationale for ambient TOAP standards. While the variety of compounds and the economic costs of TOAP control can eventually be reduced to comprehensible terms, the rationale for establishing a given TOAP standard is substantially more abstract.

The establishment of ambient standards for TOAP's involves the assessment of risks associated with exposure to TOAP's. The risk assessment process can be viewed as a mechanism to examine risks associated with exposure to air toxics so that they may be avoided, reduced, or otherwise managed. By definition, the concept of "risk" implies uncertainty. Therefore, risk assessment is largely concerned with probability: a difficult concept to grasp. Judgement is another essential part of the risk assessment process. If all judgement could be removed from the process, the risk estimates for ambient standards would be far more consistent.

Thus, the risk assessment process begins with a debatable foundation in both probability and judgement. The risk assessment process is further complicated by the fact that all of the data required to assess health risks associated with exposure to air toxics are simply not available. For example, (i) toxicity testing has not kept pace with the need for information on numerous chemicals and (ii) the environmental fate and the atmospheric chemistry of air toxics are not well defined.

Although risk assessment is, in theory, to be separate from any risk management decision, the application of professional judgement throughout the risk assessment process necessitates a sensitivity on the part of the risk assessor to risk management issues, such as the establishment of an acceptable level of risk for TOAP's. The level of risk is only one among several variables that determine risk acceptability. Deciding what level of risk ought to be acceptable is not a technical question but a value judgement. Therefore, the risk assessor must use skill, recognizing the broader ramifications when assumptions are made in the risk assessment process. The validity and usefulness of any risk assessment is tied directly to the professional abilities of the risk assessor and to the documentation of all assumptions and value judgements inherent within the risk assessment.

TOAP risk assessment focuses on cancer incidences in terms of individual risk and estimated annual incidence. Lifetime risk is an estimate of the probability of an individual contracting cancer as a result of exposure to an ambient concentration of a TOAP over a 70-year period. The annual incidence is determined by applying individual risk data, based on various exposure levels, to the entire population and then dividing by 70.

2.3. REGULATORY NEEDS

The regulatory needs for ambient air monitoring are diverse and constantly being modified. At the federal level, the statutory basis for ambient air monitoring is found in the Resource Conservation and Recovery Act and subsequent amendments, the Community Right-To-Know Act, the Toxic Substances Control Act, and the Clean Air Act. The focus and requirements of each act are different and are discussed separately in the subsections that follow:

2.3.1. Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA) was signed on October 21, 1976 and amended in 1980 and 1984. RCRA deals primarily with current and future waste handling activities. Two types of TOAP monitoring programs can be required for treatment, storage, and disposal (TSD) facilities under RCRA: First, TSD facilities may be required to establish TOAP monitoring programs as part of routine operations to safeguard community residents. Secondly, a TOAP monitoring program plan may typically be required as part of the emergency response plan for the facility.

2.3.2. Community Right-To-Know Act

The Community Right-To-Know Act of 1986 is an integral part of the Superfund Amendments and Reauthorization Act (SARA). The Community Right-To-Know Act requires emergency planning, emergency notification, community right-to-know reporting, and an emissions inventory for each affected facility. An integral component of the emergency planning requirement will be a monitoring program for TOAP's

2.3.3. Toxic Substances Control Act

The Toxic Substances Control Act (TSCA) regulates existing and new chemical substances and applies primarily to chemical manufacturers, distributors, processors, and importers. It is conceivable that TOAP monitoring programs may be required by either Section 6 or Section 8 of

TSCA. Under Section 6, EPA regulatory action can range from labelling requirements to a complete prohibition of the product if there is reason to believe that an unreasonable risk to human health or the environment is associated with the manufacture, processing, distribution, use, or disposal of a chemical substance or mixture. Section 8 addresses general reporting requirements, and under Section 8D EPA is authorized to require that manufacturers, processors, or distributors of certain listed chemicals submit health and safety data. Health and safety data may include ambient air monitoring data.

2.3.4. Clean Air Act

The Clean Air Act (CAA) requires EPA to establish national ambient air standards and national air emission standards. States are required to achieve these standards through State Implementation Plans (SIP's).

EPA designates harmful pollutants and publishes criteria documents which discuss potentially harmful effects of those pollutants. EPA then sets primary and secondary ambient air standards. Primary standards are intended to protect human health, and secondary standards are intended to protect the aesthetic values of the environment.

Senate Bill 1894 was introduced in November 1987 as the Clean Air Standards Attainment Act of 1987, as a proposed amendment to the Clean Air Act. This legislation addresses several major air pollution issues, including non-attainment areas for primary ambient air standards, interstate transport of pollutants, acid disposition, and hazardous air pollutants. With regard to hazardous air pollutants, EPA will be required to promulgate both technology-based and health-based emission standards.

2.3.4.1. Technology-Based Standards

Under Senate Bill 1894, EPA will be required to promulgate emission standards for approximately 225 compounds, of which approximately 200 are organic compounds. The entire list of compounds subject to this proposed legislation (1) is provided in Appendix A. Under the proposed amendment, EPA will also be required to establish test measures and analytical procedures for monitoring and measuring emissions and ambient concentrations of the air pollutants identified in Appendix A.

Technologically based standards will require the maximum degree of reduction in emission, based on an evaluation of costs, non-air-quality health and environmental impacts, and energy requirements. Typically, such standards will be achieved through process changes, material substitutions, process enclosures, or control equipment designed to collect, capture, or treat pollutants.

2.3.4.2. Health-Based Standards

Under the proposed amendments to the Clean Air Act, EPA is authorized to establish standards for hazardous air pollutants, on the basis of possible health impairments or adverse environmental effects. Health impairments are broadly defined as an increased mortality or irreversible or incapacitating illnesses. Chemical substances which can produce health impairments include carcinogens, mutagens, teratogens, neurotoxins, and acute and chronic toxins. With regard to adverse environmental effects, standards can be developed for compounds which exhibit adverse effects at ambient concentrations or through bioaccumulation or deposition mechanisms.

2.4. EMERGENCY SITUATIONS AND NUISANCE COMPLAINTS

Emergency response activities are primarily related to chemical spills and fires at chemical handling facilities. In such situations there exists an immediate need to conduct ambient air monitoring in the vicinity of the activity, as well as in remote areas where transport of hazardous compounds is possible. Emergency monitoring situations differ from most regulatory-related activities in several important ways: Since acute rather than chronic effects are of concern, the required detection sensitivity is less stringent. However, in many cases the exact compounds of interest may not be immediately known, and hence a broad range of monitoring techniques must be used to ensure detection of the toxic compounds. In addition, the regulatory-related monitoring activities are generally not time critical, and development of a monitoring strategy can be accomplished over a several-day or a several-week period, whereas emergency situations obviously require immediate response without development of a detailed monitoring strategy.

Nuisance complaints arising from the general public are primarily related to noxious odors, eye irritation, or in some cases, more serious illness. Monitoring activities in this regard are similar to emergency response activities in that the chemicals of interest are often not known. However, the compounds of interest may be present at significantly lower concentrations in this situation, due to the highly sensitive nature of the human senses.

2.5. AIR POLLUTION RESEARCH ACTIVITIES

Air pollution research activities require a wide variety of monitoring strategies. In general, such research activities are concerned with one of the following topics:

- Identification of toxic organics.
- Validation and refinement of sampling and analysis techniques for toxic organics.
- Development and validation of air pollution models.
- Fate and transport studies of specific organic compounds.
- Correlation of human health effects data with ambient air monitoring data.

In general, such research activities are characterized by (a) a great deal of time and effort in development of a monitoring plan and (b) the need to detect trace levels of organic compounds, if present. While many research activities are directed towards the development and support of proposed regulations, they are distinguished from regulatory monitoring activities by having a more general scope and greater flexibility.

SECTION 3.

GUIDELINES FOR DEVELOPMENT OF A MONITORING PLAN

3.1. GENERAL

The development of an appropriate monitoring plan is critical to the success of any air monitoring project. This is particularly true in the case of TOAP monitoring projects because of the low concentrations of sampled compounds and the complexity of sampling and analytical protocols.

3.2. DATA QUALITY OBJECTIVES

The first step in any planning process is the identification of objectives. EPA has embraced the process of establishing Data Quality Objectives (DQO's) as a mechanism for ensuring that the quality of environmental data collected under a given program is consistent with the intended use of that data. The DQO process is a three-stage process that places emphasis on defining the regulatory objectives of the environmental monitoring program, the decision that will be made regarding the data collected, and the possible consequences of the decision being incorrect. Experimental design based on DQO's rather than on collection of the "best possible data" is intended to ensure that the information needed to make a decision is obtained, rather then ensuring that each individual measurement obtained is the best possible.

Data quality objectives are statements of the level of uncertainty that a decision maker is willing to accept from results derived from environmental data, when the results are going to be used in a regulatory or programmatic decision such as establishing the need for a new regulation, setting or revising a standard, or determining compliance with an existing standard. Complete data quality objectives must be accompanied by clear statements of:

- The decision to be made.
- Why environmental data are needed.
- How the environmental data will be used.
- Time and resource constraints on data collection.
- Descriptions of the environmental data to be collected.
- Specifications regarding the domain of the decision.
- The calculations, statistical and otherwise, that will be performed on the data in order to arrive at the result.

The DQO process is interactive, consisting of three multi-step stages. The first two stages result in proposed DQO's with accompanying specifications and constraints for designing the data collection system. In the third stage, potential designs for the data collection program are evaluated. The various stages and steps associated with the DQO process are summarized in Table 3.1

3.2.1 Stage I Activities

This stage is the responsibility of the decision maker: He/she states an initial perception of what decision must be made, what information is needed, why and when it is needed, how it will be used, and what the consequences will be if information of adequate quality is not available. Initial estimates of the time and resources that can reasonably be made available for the data collection activity are presented.

3.2.2 Stage II Activities

This stage is primarily the responsibility of the senior program staff, using guidance and oversight from the decision maker and input from technical staff. The information from Stage I is carefully examined and discussed with the decision maker to ensure that senior program staff understand as many of the nuances of the program as possible. After this interactive process, senior program staff discuss each aspect of the initial problem, exercising their prerogative to reconsider key elements from a technical or policy standpoint. The outcome of their work, once explained to and concurred upon by the decision maker, leads to the generation of specific guidance for designing the data collection program. The products of Stage II include proposed statements of the type and quality of environmental data required to support the decision, along with other technical constraints on the data collection activity, that will place bounds on the search for an acceptable design in Stage III. These outputs are the proposed DQO's.

3.2.3 Stage III Activities

This stage is primarily the responsibility of the technical staff but involves both the senior program staff and the decision maker to assure the outputs from Stages I and II are understood. The objective of Stage III is to develop data collection plans that will meet the criteria and constraints established in Stages I and II. All viable options should be presented to the decision maker. It is the prerogative of the decision maker to select the final design that provides the best balance between time and resources available for data collection and the level of uncertainty expected in the final results.

3.3. TECHNICAL CONSIDERATIONS

There are four primary factors which shape ambient TOAP monitoring program objectives from a technical standpoint: sampling site and time frame selection, analyte selection, physical state of the analyte, and sampling and analytical protocol selection.

3.3.1. Site Selection

Selection of the appropriate sampling site(s) is an important factor in terms of developing program objectives. In some instances, such as

TABLE 3.1

COMPONENTS OF THE DATA QUALITY OBJECTIVE PROCESS

- Stage I Decision Definition
  - Responsibility: Decision Maker
  - Step 1. Decision Description
  - Step 2. Description of Information Needed for Decision
  - Step 3. Definition of Environmental Data Use
  - Step 4. Definition of Consequences of an Incorrect Decision Attributable to Inadequate Environmental Data
  - Step 5. Description of Available Resources
- Stage II Clarification of the Information Needed for the Decision
  - Responsibility: Senior Program Staff
  - Step 1. Fragmentation of Decision into Decision Elements
  - Step 2. Specification of Required Environmental Data
  - Step 3. Definition of Decision Domain
  - Step 4. Definition of Result to be Derived From Environmental Data
  - Step 5. Definition of Desired Performance
  - Step 6. Evaluation of the Need for New Environmental Data
  - Step 7. Establish the DQO's
- Stage III Design of the Data Collection System
  - Responsibility: Technical Staff
  - Step 1. Development of Viable Data Collection Plans That Meet the Criteria and Constraints Established in Stages I and II.

fence-line or spill monitoring, selection of sampling sites will be a straightforward process. In other instances, such as studying transport characteristics of certain TOAP's, site selection may be a detailed process requiring the review of extensive meteorological data and may result in the selection of many sampling sites. It is important to note that appropriate selection of a sampling site can vary with the season or over the course of the day; hence, the time frame over which samples are collected from a given site can be as important a parameter as the site from which samples are collected.

3.3.2. **Analyte Selection**

Selection of the appropriate analyte(s) is a key element of the monitoring plan. However, selection of too broad a range of compounds can lead to excessive cost, whereas selection of too few may result in non-attainment of the general program objectives. In most cases the selection of a specific set of target compounds represents a compromise between technical feasibility and environmental significance. For example, if a particular compound is emitted from a source in a given region and the program objective is to evaluate the environmental impact of that source, then monitoring of this compound is a requirement, regardless of technical limitations.

On the other hand, if a program has the objective of describing transport of TOAP's over a wide region, selection of the compounds of interest must be made with emphasis on technical feasibility. In this case, methods capable of detecting a wide range of compounds simultaneously should be employed, and compounds requiring specialized procedures should be included only if the environmental significance of the regional compounds is substantial.

A further consideration is the stability of a compound in the atmosphere: If a compound is rapidly degraded in the atmosphere through hydrolysis, oxidation, photolysis, or other processes, then one must consider the option of monitoring degradation products rather than the compound itself. Likewise, one must consider the possibility of formation of a particular compound of interest in the atmosphere. For example, formaldehyde is a common oxidation product of olefinic compounds in the atmosphere. Therefore, if one wishes to describe the impact of a source emitting formaldehyde, the formation rate of formaldehyde from olefinic materials must also be considered.

3.3.3. **Physical State of the Analyte**

The physical state of the analyte(s) will be a major concern in terms of selecting appropriate sampling and analytical protocol(s). While an analyte may be emitted as a gas, condensation of the TOAP may result in the formation of particulate or particle bound analytes. A sampling procedure designed for the collection of gaseous compounds, such as the use of a canister, will be inappropriate for particulate or particle-bound TOAP's. Conversely, a solid TOAP may have sufficient vapor pressure to require a sampling train designed for the collection of vapor phase constituents to monitor atmospheric concentrations accurately.

In most cases, the total concentration (gas as well as particle-bound) of a component is sufficient information. However, if the particle-bound concentration is of interest (e.g. for inhalation toxicology considerations) one must recognize that the data will be influenced heavily by the choice of a sampling technique.

3.3.4. Sampling and Analytical Protocol Selection

In many cases, the objectives of a program can be attained using class specific screening procedures rather than more expensive compound specific methods. Frequently, class specific or nonspecific screening techniques can be conducted in the field, often in "real time." Consequently, the use of a two-tiered (or "pilot" study) approach is often advisable, wherein these procedures can be used to rapidly define emission "hot spots," approximate concentrations, and types of compounds emitted. Appropriate compound specific techniques can then be employed to gain more detailed information.

The two-tiered monitoring approach is a simple example of using two sets of technical objectives to meet a single set of general, overall objectives. There are many other cases where overall objectives will be best attained through the sequential accomplishment of specific technical objectives. This approach allows the knowledge gained in one monitoring effort to facilitate planning of subsequent efforts. In many cases, this sequential approach may be the only viable alternative, due to information gaps or technical limitations.

Method performance characteristics should be carefully considered in the planning stage, since these characteristics have a very profound effect on the cost and probable success of a project. The specified ranges of the performance characteristics should be compatible with the intended use of the data. In certain cases, regulatory requirements may dictate the use of a specific sampling and analysis method. In such cases, project personnel should continue to evaluate the method characteristics and state any limitations impacting the success of the project.

The major method characteristics of concern are:

- Detection limit.
- Accuracy (absolute and relative).
- Precision.
- Interferences (selectivity).
- Analysis time.

Obviously, the more stringently one defines these requirements, the more costly a program becomes, often without a direct increase in useful information. Conversely, if one does not specify sufficiently rigid performance criteria, the data obtained may be of little value. Unfortunately, these performance goals are difficult to define because of the large number of determining variables (e.g. sampling location, sampling time, source composition, etc.) In addition, some of these parameters (e.g. accuracy) are difficult to determine experimentally, because the wide variation in matrix characteristics can influence them. The increased availability of Standard Reference Materials (SRM's) and improved instrumentation has resulted in increased accuracy for sampling and analytical methods. Consequently, method performance characteristics should be initially defined in terms of guideline "ranges" and should be rigidly defined only in cases where the exact requirements are known.

Required detection limits will vary considerably, depending on the compound of interest, the sampling location relative to the source, meteorological conditions, available sampling time, and available analytical instrumentation. Detection limits should always be defined in terms of component concentration in air (ug/M^3 or ppbv) rather than by a method detection limit (e.g. in micrograms), since the latter value is subject to a great deal of interpretation (e.g. sampling time, etc.) In general, the range of detection limits required for toxic organics will vary between 0.1 ppbv and 10 ppmv. Detection in the 0.1-10 ppbv range will be required for ambient air studies where sites are remote from emission sources, whereas 1-10 ppmv detection limits may be sufficient for monitoring in the vicinity of chemical spills, dump sites, and other concentrated sources. Obviously, highly toxic compounds will require more stringent detection limits in most cases.

Certain classes of compounds (e.g. halogenated compounds) can be detected at very low levels because of their unique characteristics and the availability of special detectors. Consequently, one typically obtains data on these compounds at low levels, irrespective of the project requirements. However, alternative approaches in such cases include the use of shorter sampling periods or more general procedures capable of detecting other compounds of interest. These alternatives may reduce costs without losing the desired information. Therefore, detection limit criteria should not be based solely on the available detection limit, since flexibility is lost in this process.

Some compound classes (e.g. highly polar materials such as alcohols and acids) cannot be detected readily at ppb levels. For these compounds one must decide whether or not the program objectives can be achieved using available analytical methods, toxicological properties being the primary consideration. If not, then one is left with the difficult choice of either (a) undertaking a potentially costly development program to improve the methodology or (b) reducing the program's requirements to allow partial fulfillment of its objectives or (c) not undertaking the program at all.

Accuracy and precision requirements are normally more flexible than detection limit requirements and usually do not result in a major revision of program objectives. However, several aspects of the accuracy and precision requirement need to be addressed. The required accuracy is defined primarily by the method of data comparison. If data collected on one program are to be compared to data collected on another program, then absolute accuracy is important. It is therefore important to know the accuracy of the methods used in each program.

However, if one simply desires to know the ratio of component concentration at two sites or at the same site at different times of the day, then relative accuracy may be more important then absolute accuracy. In this case, the only requirement is that the method's accuracy be the same for each data point. The relative accuracy concept is especially useful when using class specific screening techniques, since the absolute accuracy will be known only if the specific compounds giving rise to the response are known, whereas the relative accuracy is known so long as the relative proportion of the various compounds being detected is constant. In a strict sense absolute accuracy for a method can be determined only when a suitable NBS (or NBS traceable) standard is available and can be analyzed under conditions duplicating the actual sampling and analysis progress.

Precision requirements are somewhat related to accuracy requirements, since for a given atmospheric concentration the measured quantity is a function of both accuracy and precision. If one desires a certain degree of confidence that a measured signal is representative, then an appropriate number of replicate determinations must be made. The more precise the method, the fewer measurements need be made to attain a given degree of confidence in the data. Precision and accuracy will both diminish as analyte concentrations approach the detection limit.

A method's specificity and the degree of interference by other materials in a method must be considered in the definition of project objectives since this influences data accuracy as well as the range of compounds to be evaluated. If large quantities of innocuous compounds are present at the sampling location, the selection of compounds of interest, as well as sampling and analysis methods, should be based on circumventing potential interference problems whenever possible. This problem often limits usefulness of nonspecific screening procedures, since the response from background components may overwhelm any response due to trace levels of toxic materials. If such interferences cannot be avoided by judicious selection of the analyte(s) of interest, then alternative sampling and analysis procedures which minimize the interference problem must be selected. In any case, compounds which represent potential interferences in a given program should be listed, in addition to the compounds of interest, to aid in the selection of appropriate sampling and analysis techniques.

3.4. LOGISTICAL CONSIDERATIONS

A variety of logistical considerations must be evaluated in connection with the development of the TOAP monitoring program plan. These factors include the availability of manpower, instrumentation, and calibration standards. TOAP monitoring programs will typically require highly skilled personnel, non-standard methodology and/or instrumentation, calibration materials of limited availability, or a combination of these factors.

If the monitoring program objectives are to determine the ambient levels of TOAP's resulting from a temporary operation or to establish seasonal variations in ambient TOAP concentrations, it is necessary to juxtapose fixed monitoring periods with schedules for manpower, instrumentation, and calibration standards. Such a comparison will most certainly result in a modification of program objectives or of sampling and analytical protocols, if the required personnel, instrumentation, or calibration standards are unavailable during the targeted sampling period.

3.5. DATA QUALITY FACTORS

A fundamental decision that must be made during the planning process concerns data quality. The level of data quality required will be determined by, and must be consistent with, the intended use of the data. For example, if the possibility exists that the data will be used to establish or refute legal liability, then the data must be of sufficient quality to withstand legal scrutiny. If on the other hand, the data are being collected for more esoteric purposes, then a lower level of data quality may be acceptable. Program funding will impact attainable data quality and therefore must also be consistent with the intended use of the data.

3.6. COST FACTORS

A final and often overriding factor is the allowable cost. Frequently, the cost is specified within limits, prior to any other specific program objectives. While this state of affairs must be accepted, such limitations should not be used as an excuse to collect low quality data. If the specific program objectives cannot define a technically feasible and scientifically valid program, then the only valid alternative is a redefinition of scope, an expansion of available funding, or termination of the program. The impact of limitations recognized by technical project personnel must be clearly and openly stated to appropriate management personnel, in order to avoid implementation of an ill-conceived monitoring program.

3.7. COMPILATION AND EVALUATION OF AVAILABLE INFORMATION

The efficiency with which an air monitoring program can be developed and implemented is greatly dependent on the extent and quality of technical information available during the development phase of the program. In most cases this information will be used in an iterative fashion to develop specific technical objectives for the monitoring program, since such objectives must be realistic and achievable. Information most useful in this process will generally include (a) previous air monitoring data, (b) composition of emission sources in the region, (c) meteorological conditions, and (d) sampling and analytical methods and performance data for target analytes.

3.7.1. Assessment of Available Air Quality Data Base

Probably the most useful information is data from previous air monitoring programs in the region. Although such information is seldom directly relevant (e.g. due to differences in the compounds monitored, sites used, or other program objectives), some aspects of the data normally will be useful. For example, total hydrocarbon data from the region may be useful in predicting sites and/or times with maximal pollutant concentration. Data for a compound of interest may be available from a site similar to the one of interest, thereby giving an "order-of-magnitude" estimate of pollutant concentration to be anticipated.

Additional useful information which could be gained from such studies includes compound stability in air under various conditions, degradation products formed, other compounds present in conjunction with the compound of interest, phase distribution of the compound in ambient air, and performance data for sampling and analysis methods of interest. As with all sources of information, critical evaluation is necessary in order to determine the quality and relevance of the data reported.

The acquisition of air monitoring data is not particularly straightforward because of the large number of sources of such data and the wide variety of program objectives. Some primary sources of such data include:

- National Air Toxics Information Clearinghouse (NATICH).
- Air toxics monitoring data base.
- U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Regional offices of the USEPA.
- State and local environmental protection (or equivalent) offices.
- Contractors and universities performing work through contracts or grants with EPA or related agencies.
- Peer review journal articles and government reports.

A wide variety of other government and related research organizations may have available data in specialized areas (e.g. Electric Power Research Institute, Palo Alto, California; Department of Energy; National Oceanic and Atmospheric Administration).

Although a few data compilations are available, no single comprehensive source of monitoring data exists. Consequently, the best approach towards obtaining relevant data is to contact several sources (local as well as regional or national) and to describe the type of monitoring information desired. Since data specifically relevant to the program are probably not available, one should seek to obtain any potentially useful monitoring information. In many cases references within these documents may lead to additional useful data.

Critical evaluation of available data should address the following points:

- Documentation of sampling and analysis techniques, in terms of detection limit, precision and accuracy, specificity, and analysis speed.
- Sampling strategy in terms of reference points and spatial and temporal resolution.
- Documentation of atmospheric conditions.
- Influence of emission sources in the region.

The purpose of this evaluation should be to assess the relevance of the data to the program being developed; therefore, aspects of the data having no relevance to that program need not be evaluated.

Certain data bases contain much of the information required to assess the usefulness of the data for TOAP monitoring purposes. Two such data bases are described in the subsections that follow:

3.7.1.1. National Air Toxics Information Clearinghouse (NATICH) Data Base

The National Air Toxics Information Clearinghouse (NATICH) has been established by the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, to support state and local programs in the control of non-criteria air pollutants. It is intended to facilitate information exchange among state and local agencies and between EPA and those agencies and to minimize duplication of effort. For the purposes of the Clearinghouse, a toxic air pollutant is defined as any non-criteria air pollutant. Inclusion of a pollutant in the Clearinghouse does not necessarily mean that it is toxic at ambient concentrations. The Clearinghouse consists of an on-line computerized data base (NATICH) which contains information on potentially toxic air pollutants, hard copy reports of information from the data base, special reports, and a quarterly newsletter.

The NATICH data base (EPA 450/5-88-007) is updated regularly and includes a list of state and local agencies that have provided information to the Clearinghouse, air toxics contacts, regulatory program information, acceptable ambient concentration guidelines or standards and the bases of those guidelines/standards, pollutant research information, methods development activities, permitting information, source testing information, ambient monitoring information, emissions inventory information, and risk assessment information. Review of relevant NATICH data base information should be a preliminary step in the development of a TOAP monitoring program.

3.7.1.2. Air Toxics Monitoring Data Base

The Air Toxics Monitoring data base (EPA/600/3-88/010A) is a compilation of information addressing only volatile organic compounds. Semi-volatile organics, nonvolatile organics, and pesticides are intentionally excluded from the data base. The program initially focused on ambient outdoor VOC concentrations in areas remote from emission sources. It has been expanded to include residential and commercial indoor air quality data but not industrial indoor air quality data. The data base includes information relating to the Toxic Exposure Assessment Monitoring (TEAM) Program, the Toxic Air Monitoring Sites (TAMS) Program, and the Urban Air Toxics Monitoring Program.

The data base is composed of five files:

- The VOC concentration file - contains information concerning measured concentration, sampling period rankings, and ratings.

- The site file - contains information concerning the location of the sampling program.

- The methods file - provides information concerning the sampling and analytical protocol employed to generate the data.

- The reference file - contains information concerning the investigator, program objective, year of the study, and literature citations.

- The chemical file - summarizes compounds, CAS numbers, and measured concentrations contained in the data base.

Data base information can be accessed by reference, site, or chemical compound.

3.7.2. Assessment of Toxic Organic Air Pollutant Sources

Since most ambient air monitoring programs will be impacted by emission sources in the region, data concerning the composition of such emission sources are extremely useful. Programs having the objective of assessing the impact of a particular source on the environment obviously require knowledge of the source composition, whereas other programs need source emission information to avoid biasing the data, as a result of contamination by the source. Typical sources of concern include:

- Chemical production, processing, or handling facilities.

- Fuel sources (gasoline stations, storage tanks, etc.)

- Mobile sources (automobiles, etc.)

- Chemical waste landfills, lagoons, etc.

- Miscellaneous sources (dry cleaners, sewers, residential heaters, etc.)

Information concerning emission components from chemical production or related manufacturing facilities may be available from the plant operator. Discharge permits represent another source of information. Since such facilities differ widely, depending on the chemical processes contributing to the emissions, one can seldom rely to any great extent on information available from similar facilities. Furthermore, if the program objective is to assess the impact of the source on regional air quality, simultaneous measurement of the source emissions and the ambient air is highly desirable, since the composition of a single source can vary considerably with time. Knowledge of production schedules and similar factors is extremely useful in predicting the degree of variability.

In the case of fuel sources, mobile sources, dry cleaners, etc. the qualitative nature of the emissions can be predicted fairly well, since these sources have been extensively characterized, and in the case of dry-cleaners only one or two compounds (perchloroethylene or Stoddard solvent) are in use. Consequently, one can predict in advance whether or not these sources will interfere with the ambient air monitoring effort.

In general, a useful monitoring approach, assuming these source contributions are not being evaluated, is to locate sampling stations at sites remote and/or upwind from such sources (but downwind from other sources of concern), using screening techniques such as flame ionization or photoionization detection to locate the points of high source contribution. This approach requires that only the location of the source be determined, not its detailed composition. However, if the contribution of such sources to regional air pollution is being evaluated, knowledge of the detailed source composition will be required and should be made part of the overall monitoring program.

3.7.3. Assessment of Meteorological Data

Knowledge of meteorological conditions is important to ambient air monitoring programs in several regards. The impact of a particular source on regional air quality will be highly influenced by meteorological conditions, since dilution rates, transport rates, and compound stability are dependent on these conditions. Overall regional air quality, representing the summation of source contributions, will be influenced by these conditions, in the same manner.

A detailed discussion of meteorological considerations in air quality monitoring is given in the Air Pollution series by Stern (3) and is beyond the scope of this document. Meteorological parameters of primary concern include the following:

- Wind speed and direction.
- Temperature.
- Barometric pressure.
- Solar radiation intensity.
- Precipitation.
- Mixing height.

While these data should be collected during the course of the monitoring program, prior knowledge of typical conditions can be extremely useful in selecting sampling points.

Regional meteorological data can be obtained from the National Weather Service in the relevant locality. However, one must recognize that localized meteorological conditions, not apparent from the National Weather Service data, can exist. For example, wind speed and turbulence can be affected by obstructions such as tall buildings in the area. Fog may occur selectively in marshes or in hilly areas. Surveillance of the sampling site and discussions with persons familiar with the area can be useful in selecting sampling sites under favorable meteorological conditions.

3.7.4. Assessment of Relevant Sampling and Analytical Methodologies

Availability of suitable sampling and analysis techniques is often the limiting factor in the development of a comprehensive air monitoring program, in spite of the large number of techniques which exist. Since virtually every air monitoring program has a different list of compounds of interest, a variety of techniques are required to cover this range of components, resulting in a significant cost impact on the program. Furthermore, unique requirements in terms of specificity, detection limit, analysis time, and other performance characteristics may require modifications to existing methods. Consequently, a highly desirable approach is to develop program objectives which are in consonance with the capabilities of available sampling and analysis techniques, wherever possible. In order to use this approach without severely limiting the program objectives, one must have available as much relevant information as possible on sampling and analysis techniques.

Primary sources of sampling and analysis methods include the following:

- National Institute for Occupational Safety and Health (NIOSH) Methods (4).
- American Society for Testing and Materials (ASTM) Methods (5).
- Methods of Air Sampling and Analysis (6).
- Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (7).
- Peer review, journals, and government reports.

Methods for a number of toxic organic compounds of particular concern are presented in Sections 4 and 5. Contact with various persons active in air quality monitoring is also an effective means of gathering recent information on sampling and analysis methods. The NIOSH and many ASTM methods are designed for workplace or source concentrations and may require substantial modification to detect ambient concentrations.

Available sampling and analysis methods should be evaluated with regard to the following performance characteristics:

- Selectivity (range of compounds detected and potential interferences).
- Detection limit.
- Precision and accuracy (often unknown).
- Analysis time.
- Cost of analysis.
- Quality of performance evaluation data.

The methods should be evaluated from two standpoints: (a) the degree to which method performance has been documented under conditions similar to those expected and (b) the adequacy of the performance characteristics for achieving the program objectives.

If method performance is not well documented, one must decide whether or not to include further documentation, with the resultant increase in data quality as well as cost, as part of the monitoring program. A similar decision must be made when existing methods are slightly modified (e.g. extended to similar compounds, etc.) One must recognize that some assumptions concerning method performance will inherently be part of any monitoring program, due to cost and time limitations (i.e. documentation of all performance characteristics under each set of monitoring conditions is prohibitively time consuming and expensive). Consequently, those assumptions which are made should be technically sound and carefully documented.

3.8. SELECTION OF SAMPLING AND ANALYSIS METHODS

Once a set of program objectives, including specification of the analytes of interest, have been developed and information concerning sampling and analysis techniques has been evaluated, the next logical step is selection of the sampling and analysis procedures to be used in the monitoring program. Factors to be considered in selecting sampling and analysis methods include (a) physical and chemical properties of the compounds, (b) relative and absolute concentrations of the compounds, (c) relative importance of various compounds to program objectives, (d) method performance characteristics, (e) potential interferences present at site, (f) time resolution requirements, and (g) cost restraints. The selection process will be accomplished by:

- Subdividing compounds into logical groups based on similar analytical characteristics. This process will result in a preliminary selection of generic analysis techniques, since analytical techniques must be considered in the grouping process.

- Specifying detailed analytical procedures based on the guidance provided by the grouping process, considering accuracy, precision, time, and cost requirements, as well as incorporating additional cleanup schemes based on selectivity requirements, if necessary.

- Evaluating sampling procedures based on analytical requirements and physical properties of the compounds to ensure that the sampling and analysis methods are compatible.

- Specifying sampling and analysis parameters (sample volumes, final extract volumes, etc.) based on detection limit requirements.

- Reconciling conflicts between program objectives and sampling and analysis capabilities. Redefining objectives and/or undertaking procedure development efforts, as required.

- Documenting "standard operating procedures" for the sampling and analysis methods.

The important chemical and physical properties to be considered include thermal stability, volatility, polarity, ionic character, phase distribution, and chemical composition. The manner in which these properties determine the suitability of analytical as well as sampling procedures is discussed in Sections 4 and 5.

Volatility, thermal stability, polarity, and ionic character determine the extent to which commonly-used gas chromatographic procedures are suitable for the compounds. These properties also must be considered in the selection of sample preparation procedures, since solvent extraction and concentration procedures may result in loss or degradation of volatile or thermally labile compounds.

Phase distribution (gas/particle) of a compound is obviously dependent on the other physical and chemical properties but must be considered separately, since sample preparation procedures for particle bound compounds will usually be different from those for gas phase compounds. Compounds likely to be present in both phases require special consideration. Sampling methods can sometimes be employed to drive the equilibrium into one phase or the other if only the total concentration is to be determined (e.g. by using a heated filter). Methods capable of determining the phase distribution of the analyte are described in the literature (52).

Chemical composition, specifically the presence of heteroatoms, is often the most important factor in assigning compounds to a particular analytical group. Specialized chromatographic detection systems tend to be specific for a particular class of organic compounds, and selective colorimetric procedures are available for certain classes of compounds as well. However, one must avoid oversimplification of the grouping process by automatically placing compounds having a particular functional group in a single class. Individual compounds may have unique properties, making placement in another class more suitable. For example, gas chromatography with electron capture detection (GC/EC) is sensitive and selective for detection of many halogenated compounds but does not respond well to vinyl chloride, chlorobenzene, or 1,2-dichloroethane. Thus, these compounds should not be grouped with other halogenated compounds targeted for GC/EC analysis.

3.8.1. **Analytical Methodology Considerations**

Familiarity with the analytical procedures available is an obvious requirement in the compound grouping process. One must recognize that analytical procedures include both sample preparation and compound determination steps, each of which must be considered when assigning a compound to a particular analytical group. Simply specifying gas chromatography/mass spectrometry (GC/MS), for example, as the analytical technique does not define an analytical procedure.

The anticipated relative concentrations of the various compounds of interest should also be considered in the grouping process. Compounds present at high levels may be candidates for direct analysis in the field (e.g. by portable GC), since sample concentration techniques might not be necessary. At the other extreme, trace components may require sample concentration, as well as cleanup steps, to obtain sufficient sensitivity and selectivity.

A final consideration in the grouping process is the relative importance of the various compounds to the program objectives. While a formal priority ranking of the compounds normally is not required, one should consider relative importance in the following qualitative manner. Compounds of special concern, either because of high toxicity or known emission sources, should be grouped so as to optimize analytical performance for these compounds. In certain cases this process may include placing compounds of high priority in unique groups targeted for specialized, specific analysis techniques. Compounds of lesser interest should be placed in the appropriate groups selected for optimal detection of the compounds of primary concern, usually with some compendium of analytical performance.

The selection of analytical procedures is largely guided by the compound grouping process in which the available analytical techniques are heavily considered. However, the definition of analytical procedures in terms of specific operating parameters should normally await completion of the grouping process.

Relatively few standardized analytical procedures for toxic organics are available. Consequently, program technical personnel will normally have the responsibility of defining specific sample preparation procedures and chromatographic operating conditions, as well as writing the detailed standard operating procedures for the monitoring program. Factors to be considered in this selection process include required detection limit, specificity, accuracy, precision, analysis time, and cost, all of which are also considered in the development of project objectives. The task of specifying standard operating procedures for analytical methods must be accomplished in conjunction with the specification of sampling protocols, since detection limits and other method performance characteristics are a function of both steps.

Accuracy, precision, analysis time, and cost are determined by the choice of sampling and analytical techniques and, in many cases, cannot be substantially improved by refinement of the methods. Consequently one must weigh these factors carefully during the method selection process, to ensure that the program requirements are achievable using the technique selected. Method specificity can be altered to some extent by the addition of cleanup steps to the analytical methods but is still highly dependent on the type of detection system used.

Detection limits, on the other hand, can be substantially adjusted by the selection of specific operating parameters within the sampling and analytical methods. Parameters contributing to the detection limit include:

- Detector sensitivity (minimum quantity of material which gives a detectable response when introduced into the instrument).

- Proportion of sample introduced into the instrument.

- Volume of sample collected.
- Recovery of component through the entire sampling and analysis procedure.

These parameters are, in turn, dependent on other factors. Detection sensitivity is dependent on the concentration of background components in the sample (i.e. practical detection sensitivity is limited by interference from background components, not by absolute instrument sensitivity). The proportion of sample which can be introduced into the instrument is also dependent on the quantity of background components present and can be substantially increased by the use of additional or more effective cleanup techniques. Component recovery, on the other hand, can be adversely affected by the incorporation of additional cleanup techniques into the method.

3.8.2. Sampling Methodology Considerations

Because of the limited number of sampling methods available, the selection of specific sampling methods is best accomplished after the definition of analytical requirements based on compound groups of interest, etc. However, the specification of detailed analytical procedures obviously requires knowledge of the sampling scheme (e.g. physical state of the sample presented for analysis, sampling volumes, etc.).

Primary factors to be considered in the selection of sampling procedures include phase distribution, stability, time resolution requirements, and analytical requirements. Compounds entirely contained in the particle phase can be readily sampled using filtration, whereas gas phase components require more elaborate techniques such as resin sorption, impinger collection, cryogenic trapping, or evacuated canisters. Stability of the components of interest during the sampling process must be considered. If necessary, samples can be removed from the sampling apparatus and stabilized (e.g. frozen) to prevent degradation. Stability can also be affected by the collection of reactive components (SO_2, NO_x, Cl_2, etc.). Therefore, sampling techniques which minimize the collection of such components should be selected whenever possible.

Time resolution requirements may prevent the use of certain techniques which cannot acquire sufficient sample in the required time period. If extremely fine time resolution is required, continuous monitors (e.g. flame ionization or photoionization detectors) may be the only acceptable alternative. Techniques of this type are usually not specific for particular organic components, and this limitation must be weighed against the importance of time resolution.

After sampling and analysis procedures have been selected, the specific details of these methods (e.g. sampling volumes, cleanup steps, etc.) can be selected, considering the detection limit requirements in particular. Subsequently one must examine the program objectives to determine the capability of the sampling and analysis scheme to accomplish these goals. Once any differences between sampling and analysis capabilities and program objectives have been resolved, the sampling and analysis procedures should be written into detailed "standard operating procedures" as a final step in the method specification process.

3.8.3. Selection of Sampling Strategy

Selection of a sampling strategy capable of meeting the program objectives is vital to the success of any monitoring program. Parameters which must be specific include:

- Sampling locations.
- Numbers, sampling volumes, and time points of samples to be taken at each location.
- Meteorological parameters to be monitored and dependency of sampling strategy on these parameters.

The development of a sampling strategy can be extremely simple or extremely complex, depending on the program objectives. Programs involving characterization of the pollutant contribution from a point source tend to be more straightforward, whereas programs investigating fate and transport characteristics of components from diverse sources require more elaborate sampling strategies. An excellent discussion of the factors to be considered in developing a sampling strategy is provided in the Air Pollution series by Stern (8).

The selection of an optimal sampling siting plan must take into account the following factors:

- Locations of stationary as well as mobile sources.
- Transport characteristics of pollutants from these sources and influences of meteorology and topography on these characteristics.
- Spatial resolution required to meet program objectives.
- Availability of space and utilities for operating sampling equipment at potential sites.

Relevant information on optimum site selection criteria are available in various EPA documents (9). One should consult such documents when developing a siting plan.

The necessity for locating stationary and mobile sources prior to site selection has been previously discussed and should be readily apparent. One must not only have knowledge of the existence of these sources but also the trajectory of emitted pollutants under the existing meteorological and topographical conditions. Avoiding sample contamination by these sources or, conversely, accurately measuring the pollutant contribution of these sources may require continuous monitoring of meteorological parameters and adjustment of sampling location or timing, accordingly. In some cases the siting process can be aided through the use of air quality models, in particular disperson models which predict concentration profiles for pollutants emitted from point sources under various meteorological conditions. The placement of reference (control) sites upwind of known emission sources is included in most monitoring schemes to determine the contribution of those sources. Additionally, wind direction must be continuously monitored in these situations to ensure the validity of the reference samples.

Spatial resolution requirements obviously are highly dependent on the program objectives. If one is attempting to estimate pollutant concentrations in the vicinity of a point source (e.g. hazardous waste landfills), spatial resolution of a few tens or hundreds of meters may be required, whereas programs monitoring pollutant transport through an urban area may require resolution of a few miles or tens of miles. In determining spatial resolution requirements, one must realize that a sampling site provides only the concentration at a given point, and that data point is used to represent the pollutant concentration over the entire area between the sampling site and adjacent sampling sites. Consequently factors which lead to spatially inhomogeneous pollutant concentrations must be carefully considered in the siting process (i.e. spatial resolution requirements will be more restrictive in areas of inhomogeneous concentrations). Such factors include low wind velocities, presence of tall buildings and other obstacles, and source emission variability.

In certain specialized cases vertical as well as horizontal resolution is required. In most cases vertical sampling requires use of an aircraft acquiring samples at various altitudes, depending on air flow characteristics. Since this requirement is infrequently encountered in TOAP monitoring, further discussion here is not warranted.

The use of mobile sampling facilities to provide greater flexibility (e.g. in response to changes in wind direction, etc.) is an attractive option in many cases and can be a cost-effective means of providing greater spatial resolution. In many cases a continual screening monitor, such as a photoionization detector, may be used to define the need for and optimal placement of fixed monitoring stations.

A final consideration in the siting process is the availability of space and utilities for operating sampling equipment. This requirement is well recognized and does not require a great deal of emphasis in this document. Obviously, the selection of sites should be done with the knowledge of available locations and utilities. However, in cases where utilities are not readily available, portable utilities (e.g. generators, heaters, or air conditioners) must be provided. In many cases these portable units represent a potential pollution source, and hence, contamination of samples may result if their placement is not carefully considered.

After selection of appropriate monitoring locations one must consider the sampling requirements in terms of timing and numbers of samples. In many respects time resolution and spatial resolution requirements place similar demands on the sampling scheme. Continuous screening monitors can be used to determine time of dependency of pollutant concentrations and can thus define time resolution requirements more accurately. As with spatial resolution, time resolution requirements may not be uniform for a given program. Certain time periods may require finer time resolution than other time periods (e.g. related to traffic patterns, production schedules, etc.).

In order to achieve adequate time resolution, one must be able to collect sufficient sample in the allowed time. In some cases the sample quantity requirements may result in the need to use multiple sampling devices at each sampling location, although modern analytical instruments tend to provide sufficient sensitivity to obviate this situation.

The numbers of samples to be collected at each site/time point are obviously dependent on the variability of the sampling and analysis methods, the precision requirements of the program, and cost limitations. In many cases replicate analysis of a single sample, rather than replicate sampling, will be employed, in which case only analytical precision is determined. In other cases samples, collected at different times and/or sites may be treated as replicate samples, due to homogeneous spatial and temporal distribution of pollutants, hence overcoming the need to take multiple samples at each site/time point.

Sampling volume, discussed in the previous section of this document, may become a variable in the monitoring strategy as well. If pollutant concentrations varying over a wide range (not predictable in advance) or pollutants of greatly differing concentrations are to be monitored, one should consider the possibility of collecting multiple samples of varying volumes at each site/time point. In this manner one has some assurance that at least some of the samples will contain levels of analyte within the operating range of the analytical instrument. This approach is vital in certain cases when the entire sample is introduced into the analytical instrument (e.g. Tenax resin/thermal desorption techniques) and is of lesser importance when a selectable proportion of the sample is analyzed.

Meteorological parameters to be monitored usually include temperature, barometric pressure, wind speed, wind direction, relative humidity, and precipitation. Wind speed and direction are probably the most important variables impacting the sampling strategy. In many cases one may wish to sample only when the wind is in a certain direction, to take advantage of favorable source transport characteristics. In some cases meteorological parameters may impact upon spatial and temporal resolution requirements in such a manner that variations in these parameters will change the sampling strategy over time.

3.9. QUALITY ASSURANCE PLANNING

The term quality assurance (QA) refers to an overall system design to monitor, document, and control the technical performance of a program. While the need for good QA protocols is widely recognized, the design and implementation of them are frequently treated as secondary parts of the overall monitoring program. If the QA protocols for a monitoring program are to serve a useful purpose, they must (a) be readily implemented within the cost and time constraints of the program and (b) be well understood by the project personnel. Preparation of the QA plan for a monitoring program should be undertaken after the sampling strategy and the sampling and analysis methods have been defined.

An effective QA plan for a TOAP monitoring program must address five basic areas: (a) quality assurance management, (b) sampling quality assurance, (c) analytical quality assurance, (d) data reduction quality assurance, and (e) reporting quality assurance. Specific considerations for quality assurance activities in each of these five key areas are summarized in Table 3.2. Each of these topics is addressed thoroughly in Section 7.

A series of volumes entitled Quality Assurance Handbook for Air Pollution Measurement Systems (10) serves as a useful, detailed guidance document in the QA area. In particular, Volume I - Principles and Volume II - Ambient Air Specific Methods may be useful in the field of toxic organic monitoring. Specific guidance for preparation of QA plans is provided in another EPA document (11). QA practices are also discussed in Methods of Air Sampling and Analysis (6).

3.10. DEFINITION OF DATA REPORTING FORMAT

Many air monitoring programs are undertaken without prior definition of the data reporting format. In some cases this approach is justified because of the unexpected nature of the data obtained (e.g. unexpected compounds detected or previously unknown sources identified). However, to the extent possible the format for data presentation should be defined prior to initiation of the monitoring effort. This practice helps to identify limitations of the available data and further clarifies the extent to which technical and management or policy personnel understand the program objectives.

The optimal format for data presentation is obviously highly dependent on the program objectives and the quantity of data obtained. In cases where only a few data points are obtained around a point source (e.g. a hazardous waste landfill) tabular presentation of data (compound concentrations at each site) may be appropriate. However, in most monitoring situations the quality and complexity of the data set will require graphical presentation. This type of data format requires definition of the important variables to be considered (e.g. source locations, sampling times, sampling sites, meteorological effects, etc.) Statistical methods for evaluating correlation between the important variables are usually required to obtain meaningful conclusions from the data set.

3.11. SAFETY CONSIDERATIONS

Safety considerations in air monitoring are similar to those for other chemically related occupations but should be considered for each air monitoring program, since unusual hazards may be present in these situations. Potential safety hazards can be subdivided into the following broad categories:

- Chemical hazards.
- Electrical equipment.
- Mechanical equipment.

TABLE 3.2

QUALITY ASSURANCE (QA) ACTIVITIES TO BE SPECIFIED IN PROGRAM PLAN

Quality Assurance (QA) Management

- QA System Design.
- Document Control.
- Data Evaluation and Storage.
- Audit Procedures.
- Corrective Action.
- QA Reports to Program Management.
- Training.

Sampling Quality Assurance

- Site Selection.
- Instrument Calibration and Maintenance.
- Collection of Routine Quality Control Samples.
- Data Recording.
- Sample Labeling, Preservation, Storage, and Transport.
- Chain of Custody Procedures.

Analytical Quality Assurance

- Method Validation Requirements.
- Instrument Calibration and Maintenance.
- Quality Control Sample Analysis.
- Data Recording.

Data Reduction Quality Assurance

- Merging Sampling and Analysis Data Files.
- Storage of Raw and Intermediate Data.
- Data Validation.

Reporting Quality Assurance

- Technical Review of Report.
- Editorial Review of Report.

Chemical hazards include toxic chemicals such as carcinogenic compounds, corrosive chemicals such as concentrated acids or bases, and explosive hazards such as compressed gases. Protective equipment should be employed to minimize direct exposure to such hazards. Since most air monitoring programs require working with concentrated standards of toxic organic compounds, special emphasis should be placed on minimizing exposure to these materials. Programs involving investigation of concentrated or potentially concentrated sources of hazardous organic compounds require additional safety protocols to protect workers in the field as well as laboratory workers who could be unexpectedly exposed to concentrated samples collected at such sites.

Hazards from corrosive chemicals, compressed gases, glassware, mechanical equipment, and electrical equipment are presented in a variety of safety texts and do not require special emphasis here. However, these hazards should be addressed in the monitoring plan.

3.12. MANPOWER REQUIREMENTS

A significant amount of discussion has been directed at the many elements that comprise an effective monitoring plan. It is important to remember that properly trained personnel with appropriate levels of experience must be available when needed, to ensure the success of the monitoring program. Personnel may be involved with several simultaneous projects, so it is important that careful attention be given to personnel scheduling, to ensure that no project suffers due to unavailability of human resources.

SECTION 4

OVERVIEW OF SAMPLING METHODS

4.1. PHYSICAL AND CHEMICAL PROPERTIES

The selection of an appropriate sampling technique is a crucial decision that significantly impacts the success of a monitoring program. The sample collection process is often one of the major sources of error in determining concentrations of atmospheric toxic organics. An obvious initial consideration is that of the physical and chemical characteristics of the compound(s) of interest. Selection of the most effective collection apparatus based on the analyte's specific physical and chemical profile should be the sampling method selection objective.

Physical properties to be considered include boiling point, vapor pressure, polarity, and solubility in water and organic solvents. There are several good handbooks (12, 13, 14, and 15) which can be consulted to obtain information concerning the physical and chemical properties of organic compounds.

Ambient air contains a complex range of trace level organic compounds which have diverse physical and chemical characteristics. For simplified further discussion, they have been grouped into the following categories based on their degree of volatility.

4.1.1. Volatile Organic Compounds

Volatile organic compounds (VOC) is a general term used to describe the gaseous non-methane organic emissions from a variety of sources. These compounds have vapor pressures greater than 10^{-2} kPa and thus are predominantly found in the gaseous state in the atmosphere. Much of the present work dealing with organic compounds in air has been done on VOC's because they allow for high volume sampling and can be efficiently thermally desorbed from the sample collection medium.

Sampling with solid sorbents is one of the most widely used methods for VOC collection. Typically, large volumes of air are passed through a sample train containing several cartridges of an inert adsorbing material such as Tenax^{R}, XAD-2, or Porasil^{R}. The organic constituents are adsorbed and concentrated on the sorbent surface. Unfortunately, solid sorbents are not compound specific; analyte breakthrough can occur; and all organic compounds may be collected. Separation is usually accomplished by thermal desorption or solvent extraction, followed by gas chromatographic analysis. A wide variety of solid adsorbents are available and have been used and determined to be appropriate for specific needs. These will be discussed in more detail in Section 4.2.1.

Canister-based sampling systems have been evaluated and improved for collecting VOC's. Comparisons between Tenax^R and canister collection has been conducted (16,17), and comparative guidelines have been developed which yield statistical inferences as to the equivalency of the two sampling techniques. As a result of these developmental efforts, commercial canister-based ambient air samplers are now available.

Other methods which continue to be modified to collect VOC's more effectively include cryogenic condensation, impinger collection, derivatization techniques, and passive samplers. While these methods are promising, sampling systems which employ either solid sorbents or evaluated canisters represent the standard for VOC sampling work.

4.1.2. Semi-Volatile Organic Compounds

Semi-volatile organic compounds (SVOC's) are not as easily collected for analysis as the VOC's. However, attention has been focused at resolving the problems associated with SVOC's found in ambient air. Members of this class include polynuclear aromatic hydrocarbons (PAH) with four or fewer fused rings, their halogenated derivatives such as PCB's, organopesticides with chlorine and phosphorus, and various chloro-p-dibenzodioxins. Vapor pressures of these compounds range from 10^{-2}kPa to 10^{-8}kPa. These less volatile compounds are present in the atmosphere, both in the gaseous phase and in a particle-bound phase. This presents the problem of quantitative collection requiring phase distribution analysis. Attempts at vapor-particle distribution determination have been made with uncertain success.

An effective sampling system for SVOC's employs a quartz (or other low background) filter substrate followed by a vapor trap. The components of interest are desorbed from both the filter and the vapor trap and analyzed for SVOC content. It is incorrect to assume, however, that the SVOC found in the filter represents the entire particle-bound phase while the concentration of SVOC desorbed from the vapor trap comprises the gas phase SVOC. Some SVOC will be transferred from the particle-bound phase to the vapor trap during the sampling process. The distribution between phases is also dependent on temperature and the degree of volatility of the compound(s) of interest. For these reasons phase distribution analysis is a complex determination. This will be discussed further in Section 4.4.

A side-by-side sampling comparison of Amberlite^R XAD-2 resin and polyurethane foam (PUF) revealed XAD-2 has better collection and retention efficiency for small ring SVOC (18). Both foam and resin performed well on larger, less-reactive compounds.

Several works have adapted current high volume air sampling methodology to collect SVOC's; see for example Reference 19 and Method TO-9, Reference 7: Sampling and Analysis of Chlorinated Dibenzo-dioxins and Furans.

A data base for the chemical, physical, and thermodynamic properties of 720 polycyclic aromatic compounds (PAC) has been compiled on personal computer discs, using SCIMATE data management software (20). This information can be useful in the selection of a sampling method.

4.1.3. Nonvolatile Organic Compounds

Ambient air contains relatively low amounts of nonvolatile organic compounds (NVOC). These are compounds with vapor pressures less than 10^{-8} kPa, and are almost always found in the condensed particle-bound state. Polynuclear hydrocarbons with more than four rings, and their nitrogenous and oxygenated derivatives are the major constituents of this category (21). The predominant method for measuring NVOC is collection using a high volume filtration device followed by solvent extraction. A system of this nature has been described in detail (22).

4.2. METHODS FOR GAS PHASE COMPONENTS

Compounds which are predominantly in the gas phase at ambient temperatures and pressures are generally sampled by passing the air sample through a filtration device to remove the particulate matter before subsequent capture of the gaseous compounds. In selected cases, direct analysis of the filtered gas stream is possible, circumventing the need for the capture and/or pre-concentration process (e.g. direct GC with /FID or ECD) (23). This situation is rare in ambient air monitoring for toxic organics because the low concentrations generally make pre-concentration of the sample a necessity. A general discussion of various sampling approaches for gas phase components is provided in Katz's book (24).

4.2.1. Solid Adsorbents

Solid adsorbents are the most frequently used sampling media for gas phase organics in ambient air because they allow a large volume of air to be sampled relative to other techniques. Solid adsorbing materials can be grouped into three categories:

- Organic Polymeric Adsorbents.
- Inorganic Adsorbents.
- Carbon Adsorbents.

4.2.1.1. Organic Polymeric Adsorbents

Tenax^{R} GC is a porous organic polymeric adsorbent that has probably been used and researched more than any other material for the purpose of organic gas sampling. Initially introduced as a GC column packing material, its inertness, low affinity for water, and high thermal stability make it an excellent adsorbent for most volatile organic compounds with molecular weights ranging up to several hundred AMU.

Performance audits conducted on sampling systems using Tenax^{R} cartridges have revealed inconsistencies which necessitate precautions and adherence to quality assurance procedures to minimize error (25,26). Tenax^{R} GC requires thorough conditioning prior to use in order to minimize contamination. This is accomplished by simultaneously purging the cartridge with an inert gas and heating the gas to a high temperature. Tenax TA, a specially processed Tenax, is specifically designed as a trapping agent with very low levels of potentially interfering impurities; however, conditioning is still recommended for Tenax TA. (Interference due to toluene and/or benzene is a common problem associated with improperly conditioned or aged Tenax.) It should be noted that conditioning of the adsorbent does not completely eliminate the problem of interference. Other complications are also encountered with solid adsorbents. For example, artifact formation resulting from reactive air components such as ozone, NO_x, and SO_x interacting with organic compounds or the sampling media may occur during sampling, storage, or the recovery process. Thermal degradation of the polymer matrix resulting in the production of detectable levels of interferents is another problem associated with Tenax.

Another limitation of this technique is the fairly low breakthrough volumes (the volume at which the analyte species begins to elute from the sorbent during sampling). Sample volumes are therefore required to be less than the smallest breakthrough volume for the compounds of interest, and backup cartridges are required. While breakthrough volumes have been studied for individual compounds, complex interactions occur when many species are present. These interactions generally lower breakthrough volumes determined from pure materials and introduce considerable uncertainty in the selection of sample volumes.

For these reasons, solid sorbent sampling trains designed for simultaneous collection of samples at different flow rates are often employed. This approach, termed "distributed air volume sampling," identifies samples which may have been adversely affected during the sampling, storage, and desorption process. The recommended procedure uses a set of four samplers simultaneously collecting different volumes of air (e.g. sample volumes of 10-15L, 20-30L, 40-60L, and 80-100L are recommended for Tenax). Comparison of the four data sets can result in the identification of problems associated with sample collection, storage, and/or sample desorption. It is also important that the sampling and analysis scheduling be thoroughly coordinated to permit prompt analysis.

XAD^R resins are another popular solid sorbent. When coupled with a quartz prefilter, XAD resins are superior to polyurethane foam (PUF) for polyaromatic hydrocarbon sampling (18). There are fewer problems associated with PAH breakthrough, loss, and degradation when XAD^R resins are used. The retention characteristics and sorbent capacities on XAD-2 resin for many chemicals are provided in EPA publication 600/7-78-054.

Polyurethane foam (PUF) is another organic polymeric adsorber that has been used for collection of SVOC pesticides, polychlorinated biphenyls (PCB's), and dioxin vapors. Low volume sampling with PUF is utilized in Method TO-10 for the analysis of pesticides. The PUF cartridge is easy to use and has good air flow characteristics. EPA has evaluated the use of PUF samplers and three cleanup methods associated with them (28). The cleanup methods are compression rinsing, Soxhlet extraction, and a combination of both. Results indicate compression rinsing alone is sufficient for contaminant removal prior to sampling.

Styrene copolymers have been studied as air samplers. Benzene and acetone breakthrough volume determinations have been performed on Poropak Q and Chromosorb 101, 102, and 103 (29).

These are a few of the many porous polymers used frequently for air sampling because of their many desirable advantages. One major disadvantage of polymeric sorbents is the inability to capture highly volatile organic compounds such as vinyl chloride and certain low molecular weight polar compounds (21). A modified polymer material (Eu-sorb^R) has been developed which specifically captures very volatile polar organic compounds such as aldehydes, ketones, and nitriles by forming a metal complex. A comparison between the metal chelating Eu-sorb^R with Tenax TA and Chromosorb 102 revealed Eu-sorb^R to have large breakthrough volumes and to be more efficient at pre-concentrating highly volatile polar organics (30). Its use has been limited, but potential applications are promising.

4.2.1.2. Inorganic Adsorbents

Inorganic adsorbents include silica gel, alumina, Florisil^R, Porasil^R, and inorganic molecular sieves. These materials are considerably more polar than organic polymeric sorbents and thus capture polar compounds. Water can be efficiently captured on certain media and result in deactivation of the material. Consequently, these adsorbents are rarely used to collect trace organic compounds, except in cases where relatively high concentrations of certain polar organics are prevalent. Silica gel will adsorb compounds with hydroxyl groups such as alcohols and phenols and other oxygen-containing compounds such as esters, aldehydes, ketones, and organic esters. Florisil^R has been used to collect chlorinated pesticide residues with consistent recoveries. Inorganic adsorbents offer one advantage over organic adsorbents in that the organic substrate is less likely to be a source of organic interference.

4.2.1.3. Carbon Adsorbents

Carbon adsorbents are relatively nonpolar compared to the inorganic adsorbents; thus, water adsorption is a less significant problem. However, water adsorbtion may still prevent analysis in certain applications. The carbon based materials tend to exhibit much stronger adsorption properties than organic polymeric adsorbents, hence allowing efficient collection of highly volatile materials such as vinyl chloride, benzene, and toluene. However, the strong adsorption on carbon adsorbents can be a disadvantage in cases where recovery by thermal desorption of less volatile materials such as benzene or toluene is desired because of the excessive temperatures required (e.g. 400° C).

There are a variety of carbon based adsorbents available with widely varying adsorption properties. The commonly available classes of carbon adsorbents include:

- Various types of conventional activated carbons.
- Carbon molecular sieves.
- Carbonaceous polymeric adsorbents.

Conventional activated carbons have a microporous structure which leads to difficulty in recovering adsorbed materials; therefore this material is rarely used in trace organic sampling.

Carbon molecular sieves have a spherical, macroporous structure which theoretically leads to better recovery of adsorbed materials, relative to conventional activated carbons. These materials are sold under various trade names (e.g. Spherocarb, Carbosphere, Carbosieve, and Ambersorb XE-347) and have been used to a limited extent for the determination of volatile organics such as vinyl chloride and methylene chloride (31). TOAP monitoring data using carbon molecular sieves have been inconsistent, and leading investigators are diverging from this sampling approach.

Carbonaceous polymeric adsorbents are described as hard, non-dusting spheres with properties intermediate between activated carbon and organic polymeric adsorbents. These materials are available from Rohm and Haas Chemical Company under the trade name "Ambersorb" (XE-340, XE-347, XE-348). Of the three materials, Ambersorb 347 is classified as a carbon molecular sieve; XE-348 is most similar to activated carbon, and XE-340 is most similar to organic polymeric adsorbents. XE-340 appears to have some attractive features in terms of trace organic sampling and has been shown to be useful for volatile compounds in the C_4 to C_6 boiling point range (32,33), a volatility range not covered by organic polymeric adsorbents such as Tenax.

Carbon hollow tubes (CHT's) have been introduced as pre-concentrators of atmospheric organic compounds (34). They have been shown to be stable for compounds with boiling points between 90°C and 235°C. The design eliminates many problems associated with other materials. The adsorbent surface is shallow and allows for rapid thermal desorption, perhaps minimizing decomposition of trapped analytes. Also, rapid desorption makes direct interfacing with GC feasible. Finally, the open tubular design provides a high degree of separation of gases and particles.

In selecting particular adsorbent materials for sampling trace organics, one must consider both the capture process and the compound recovery process. Generally, either thermal desorption or solvent extraction is employed to recover the analytes. Thermal desorption is most useful for compounds having boiling points of less than 300° C, whereas solvent extraction is most useful for compounds boiling above 150° C. The decision on which methodology to use for those compounds which boil between 150° and 300°C should be based on characteristics of the compounds within this range. The actual upper bonding point limit for thermal desorption is also dependent on the temperature limitations of the sorbent used for sampling.

Thermal desorption is an attractive approach in many cases because the entire sample can be introduced onto the analytical instrument. This can be a disadvantage, however, because multiple analyses using the same sample are difficult to perform. Should the analysis equipment fail or the working range of the procedure be exceeded, no data can normally be recovered. For this reason multiple samples are typically collected at each sampling site to minimize the impact associated with the loss of a sample during analysis. Since levels of organic contamination are often very low, these disadvantages are less significant than the enhancement of detection limit. Furthermore, the thermal desorption process is more readily automated and does not require disassembly of the sampling cartridge prior to analysis.

When solvent extraction is used, only a small fraction of the extract (e.g. 1-10 percent) can be introduced. This advantage allows adjustment of the concentration of analyte introduced into the analytical system (i.e. the analyte remains within the working range of the instrument) and also allows for replicate analysis of a sample, which can be an important consideration. Use of solvent extraction also avoids the problem of thermal decomposition of labile compounds during the analysis step.

The use of supercritical fluid extraction with CO_2 of Tenax-GC sorbent traps to yield rapid and quantitative recovery of PAH's has been demonstrated for compounds with molecular weights as high as 300 AMU at low temperatures (45° C). This technique may provide a viable alternative to liquid solvent extraction and thermal desorption.

Although a wide variety of approaches employing solid adsorbents may be feasible for any given monitoring situation, the following summary offers useful guidance for generalized cases:

- Thermal desorption of organic polymeric adsorbents (especially Tenax GC) is useful for compounds boiling between 60°-300° C, exclusive of highly polar compounds such as methanol and acetone.

- Solvent extraction of organic polymeric adsorbents (especially XAD-2) is most useful for compounds boiling above 150° C and can in some cases be extended to more volatile compounds, depending on solvent and mode of concentration.

- Thermal desorption of carbon adsorbents (especially carbon molecular sieves or Ambersorb XE-340 and CHT's) may be useful for volatile compounds boiling in the range 0°-70° C, including vinyl chloride. However, the high temperatures (350°-400°) required for desorption from these media may lead to degradation of many labile compounds. If medium or high concentrations of compounds are of concern, solvent desorption of carbon adsorbents may be a useful alternative.

- Supercritical fluid extraction of solid adsorbent (Tenax GC) by CO_2 is a useful alternative for recovery of PAH's at low temperatures. The potential for class selective extractions and direct coupling with on-column cryogenic trapping in a gas chromatographic column exists.

- Inorganic adsorbents such as silica gel or alumina are not generally useful for ambient air monitoring, because of the water deactivation problem. However, when high concentrations of polar organics are a concern, they may be the method of choice, since they have high affinities for these materials, which can usually be recovered by solvent extraction.

4.2.2. Whole Air Collection

Collection of whole air samples by means of evacuated glass bulbs, stainless steel canisters, Tedlar^R bags, or other devices is probably the simplest sampling approach and can be useful in many situations. Grab sampling advantages have been discussed by Krasnec (36). One major concern with this type of sampling is the loss of analyte due to adsorption and permeation through the container walls. At very high concentrations (e.g. several ppm) condensation may also be a problem. Consequently, this approach has been utilized primarily for highly stable compounds such as hydrocarbons and chlorinated hydrocarbons with boiling points less than 150° C. Long-term storage of certain compounds usually results in loss of analytes.

4.2.2.1. Glass Sampling Bulbs

Containers for whole air sampling can be categorized as rigid or non-rigid devices. Evacuated glass bulbs are rigid devices that have been used extensively in the field. They are convenient, easy to handle, and relatively inert sample containers. Their main disadvantage is their susceptibility to breakage, especially during transportation.

4.2.2.2. Gas Sampling Bags

Bag collection of airborne analytes is commonly employed. Trade names include Tedlar, Teflon, Mylar, and Saran. Generally bag sampling is used for short-term storage and analysis occurring within a few hours. Leakage and/or permeation of materials into and out of the bag is a common problem, and trace level concentrations will not allow for such losses. On the other hand, bags are advantageous for being lightweight and easily transportable. Reuse of gas sampling bags is not recommended when sampling for very low levels of organics. When bags are reused they must be rigorously cleaned by multiple evacuations and fillings. The cleanliness of each bag should then be established before use. Even new bags can be a source of contamination and their cleanliness should be established by blank analysis prior to use. The standard of cleanliness will be determined by the concentration of the analyte to be measured and the analytical method.

4.2.2.3. Summa^R Polished Canisters

Stainless steel canisters which have been passivated by deposition of a pure chrome-nicked oxide on the interior surface (Summa^R polishing process) offer many advantages for VOC and SVOC sampling.

The canisters are not subject to sample permeation or photo-induced chemical effects, and they can be reused after a simple cleanup procedure. The sample integrity of trace level organic compounds stored in Summa polished canisters has been summarized (35) for storage periods up to 30 days. A study also revealed that canisters which had been subject to many sampling/cleaning cycles performed better than new canisters, which showed trace level contamination on an initial blank test.

Side-by-side comparison of sampling with Tenax GC and passivated canisters has also been conducted (16), yielding satisfactory results. Canister sampling offers a distinct advantage over sorbent sampling in that artifact formation, high blank, and background values, and sorbent capacity problems are eliminated. Additionally, because a whole air sample is collected into the canister, this sampling procedure is applicable to compounds with a much broader range of boiling points and vapor pressure.

A prototype sampler system to collect and transfer VOC's from ambient air has been designed (38), which uses Tenax to adsorb and desorb organic compounds and then transfer them to storage canisters. Sample enrichment (15- to 35-fold) is achieved by utilizing less volume flow in the desorption step than in the adsorption process. This demonstrates the feasibility of a non-cryogenic pre-concentration technique that can be used with stainless steel canisters and that still provides adequate sample enrichment. Obviously, limitations of this procedure are still those associated with the use of solid sorbents.

Pre-evacuated canisters are used for sampling in one of two ways. For subatmospheric sampling, an evacuated canister is used to collect a sample until the pressure of the canister approaches atmospheric pressure. For pressurized sampling, gas is pumped into an evacuated canister until the pressure in the canister reaches 15-30 psig. The method which employs canisters (TO-14) has been most extensively documented using pressurized sampling techniques.

4.2.3. Cryogenic Trapping

The collection of atmospheric organics by condensation in a cryogenic trap is an attractive alternative to adsorption or whole air collection. The primary advantages of this technique include:

- A wide range of organic materials can be collected.
- Contamination problems with adsorbents and other collection media are avoided.
- The sample is immediately available for analysis (direct interfacing with GC possible).
- Consistent recoveries are generally obtained.

However, an important limitation of the technique is condensation of large quantities of moisture and lesser amounts of certain reactive gases (SO_2, NO_x, etc.)

Cryogenic sampling can be accomplished in a variety of ways, depending on the desired detection limit and compounds of interest. The important parameters to be specified include:

- Choice of cryogen.
- Trap design.
- Method of sample recovery.
- Method of analysis.

Useful cryogens include liquid oxygen, liquid argon, dry ice-solvent systems, and ice water. Liquid nitrogen is not an acceptable cryogen because large quantities of air will condense. Ice water is not cold enough for collecting organics in ambient air, except for relatively nonvolatile compounds. Dry ice-solvent systems should be employed with caution because of the high probability of contaminating the sample with relatively large quantities of solvent. Liquid oxygen or argon appear to be the most generally applicable cryogens, although the safety hazards associated with liquid oxygen make its use less attractive.

The design of a suitable sample trap is extremely important in cryogenic sampling. One must ensure that the air residence time in the trap during sampling is great enough to allow for cooling of the gas stream and condensation of the analyte of interest. The trap material must be able to withstand the wide temperature range involved in the sample process. The trap design must also be appropriate for the sample recovery step, allowing efficient recovery without loss or contamination of the sample. For highly volatile materials, the inclusion of an adsorption medium such as silica gel may be necessary to obtain satisfactory collection efficiency.

Cryogenically collected samples can be recovered either by flash evaporation into an analytical instrument or by solvent flushing of the trap. The former approach is preferable in most cases because it allows more sensitive detection and avoids contamination (e.g. from solvents). However, the solvent flushing approach can be accomplished with less elaborate equipment in the field and may be preferable for the analysis of higher concentrations of material.

A new technique has been developed that resolves some of the problems associated with both cryogenic and porous polymer sampling techniques and utilizes the desirable characteristics of each. This method involves cryogenic concentration followed by volatilization and transfer in an inert gas stream to Tenax tubes to avoid analyte breakthrough and artifact formation problems. The technique should be applicable for determination of VOC's with a wide range of volatiles.

A simplified cryogenic pre-concentration, direct flame ionization detection (PDFID) method for non-methane organic compounds in ambient air (Method TO-12) has been developed and recommended for use by state and local air pollution control agencies in the development of their ozone control plans (40).

A cryogenic sampling approach for monitoring trace organics in ambient air has been described (39), which involves the use of a small (3 mm ID) trap packed with silanized glass beads and held at liquid argon or liquid oxygen temperature. A 50-500 ml volume of ambient air is drawn through the trap by means of an evacuated tank/manometer assembly as the pumping and volume measurement system. The trap is directly connected to a six-port stainless steel valve, and following sampling collection the condensed material is flash evaporated onto a capillary GC/FID system for analysis. Detection limits on the order of 0.5 to 1 ppbv can be achieved using this approach. Even lower detection limits can be achieved for certain compounds by the use of selective detectors such as an electron capture detector (ECD). This technique requires transport of the analytical system to the monitoring site or collection of a whole air sample in an evacuated cylinder, with subsequent laboratory analysis. For higher boiling compounds adsorption onto container walls may represent a significant problem if the latter approach is employed.

4.2.4. Impinger Collection

Impinger or "bubbler" collection involves passing the gaseous sample through a liquid adsorbing solution and "scrubbing" out the species of interest. Aldehydes and ketones may be sampled with a liquid impinger system using DNPH reagent for subsequent HPLC analysis (Method TO-5). All glassware should be thoroughly rinsed with methanol and oven dried before use. Sodium hydroxide liquid impinger collection for creosol and phenol is used in EPA Method TO-8. With the exception of Methods TO-5 and TO-8, impinger based sampling systems have limited applications to TOAP monitoring programs because large volumes of air must be sampled, resulting in solvent evaporation, to achieve required detection limits.

4.2.5. Derivatization Techniques

With the exception of canister based sampling systems a fundamental limitation of the various sampling techniques discussed so far is the decomposition of reactive compounds during sample collection or transport. Two approaches can be used to circumvent this problem. One obvious approach is to use a direct analysis technique in which the analyte concentration is determined without physically isolating the air sample (e.g. total hydrocarbon analysis).

An alternate approach, discussed in this section, is to stabilize reactive compounds by combining them with a derivatizing reagent during the sampling process. In many cases derivatizing reagents can be chosen which not only stabilize the compound but enhance its detectability. Such schemes are available for determining formaldehyde (TO-11), aldehydes (TO-5), phosgene (TO-6), and certain other reactive compounds.

In certain cases, such as the 4-aminoantipyrene method for phenols and the ninhydrin method for amines, the derivatization step is used solely to enhance detectability and may be done in the laboratory rather than the field. In this section, only derivatization techniques for field use are considered. Derivatization schemes for specific compounds or compound classes are discussed later.

Derivatization reagents for field use can be held either in an impinger or on a solid adsorbent. The impinger approach is most convenient because reagents can be prepared and stored as liquid solutions, whereas solid adsorbent systems require more elaborate preparation and storage procedures. However, the solid adsorbent approach is more sensitive in many cases because larger volumes of air can be sampled. A study of both these approaches for aldehyde derivatization has been reported (42). In this particular example, the impinger approach appears most useful because it provides adequate sensitivity and is less susceptible to humidity effects on analyte recovery.

All derivatization techniques require the use of high purity reagents. Normally, fresh stocks of reagent should be prepared for each sampling episode or more frequently if degradation or contamination (through passive diffusion of materials into the reagent) is a problem. One must be aware of potential interference in the method, especially from reactive gases present at high levels in the sample (e.g. water, SO_2, NO_2, O_3, etc.) and must incorporate quality control procedures to ensure such interferences are not a problem.

4.2.6. Passive Samplers

In recent years, the development of passive sampling devices (PSD) has drawn much attention. These devices sample by means of diffusion or permeation rather than by means of a pump. They have been shown to be simple, convenient, inexpensive, and valid alternatives for assessing time-weighted average concentrations for personal exposure monitoring (43).

Analysis of adsorbed compound is accomplished by thermal desorption and chromatographic separation. Specificity can be introduced into a passive sampling technique by a suitable choice of adsorbent substrate (44). A passive sampler using a DNPH-coated glass fiber filter has been developed for formaldehyde (45). A comparison of recoveries of trichloroethylene from active charcoal tubes and a thermally-desorbable personal monitor revealed the passive sampler to exhibit better recovery efficiency (46). A personal dosimeter based on molecular diffusion and direct detection by room temperature phosphorescence has been developed to monitor vapors of polynuclear aromatics (47).

4.2.7. Direct Analysis

Probably one of the most attractive sampling and analysis approaches is that of direct measurement, requiring no sample collection, storage, and transfer. Methods for organic compounds fitting this definition include colorimetric, spectroscopic, ionization and other related techniques. Specific techniques are discussed in detail in the section on field screening techniques in Section 5. One major limitation of these techniques is their lack of sensitivity, because the sample is not preconcentrated.

Problems such as analyte degradation and adsorptive losses are not a factor in direct analysis because the sample is immediately analyzed in the field. Delivery of the sample to the analytical device is usually through an inert and heated sample line (Teflon or passivated stainless steel). A heated filter is typically placed upstream to collect interfering particulate matter. Carbon monoxide and water present in the atmosphere may sometimes cause interference but can be eliminated by use of an adsorber/collection trap upstream from the analytical device.

4.3. METHODS FOR PARTICULATE AND PARTICLE BOUND COMPONENTS

Many SVOC's and polar organic compounds in ambient air are associated with solid particulate matter dispersed in the atmosphere. These organic compounds may adsorb or condense to different degrees and exist in a complex, dynamic, solid-vapor equilibrium with particulate matter. Sampling for trace organics in air almost always alters the solid-vapor interphase, making determination and adequate representation of the ambient condition difficult. Particulate collection is usually accomplished by filtration, centrifugation, impaction, or electrostatic precipitation, all effective for collecting solid matter down to sizes in the micrometer range. During the capture process certain components may be driven by air flow through the sampling system from the particle-bound phase to the gas phase and some of the gaseous components may adsorb or react on the filter media. Additional interference may result from artifact formation or photochemically induced changes when organic and inorganic components are concentrated on sampling media. Consequently the particle-bound concentration of an analyte is an operationally defined term and must be chosen to satisfy the program objectives. These considerations will be conditional upon the organic species of interest and their physical characteristics.

One aspect of particle sampling for trace organic analysis is the need for a gas phase collection device (e.g. adsorbent, impinger, etc.) downstream from the particulate capturing device. Analysis of both collection media will be necessary for total analyte concentration but may not reflect the actual phase distribution at ambient conditions. Gas and solid phase distribution will be discussed in more detail in the following section, and a good coverage of sampling considerations for particulate matter is given in Stern's book (48).

4.3.1. Filtration

The most common method for collecting particulate matter is filtration, due to its low cost and simplicity. A wide range of filter media with diverse permeation characteristics is available. If only the total quantity of organic analyte is of interest, the filter may be operated at an elevated temperature (above 150° C) to vaporize the material so that the analytes can be collected in the gas phase, hence simplifying the analysis requirements. This can however, result in analyte loss via degradation or interferent production via artifact formation. If the particle-bound concentration is to be determined, the sampling system should be maintained at ambient temperature conditions, and the sample volume should be minimized to reduce volatilization. Unfortunately, the low levels of ambient particulate matter usually require the collection of several hundred cubic meters of air (e.g. with a high volume sampler). Under these conditions even relatively nonvolatile compounds (e.g. three- and four-ring PAH's) may be lost to some extent. Chemical transformation of some adsorbed material through reactions with atmospheric inorganic gases (e.g. NO_x, SO_2, and O_3) can also be a problem in certain situations.

The most commonly used filter media for sampling organics are:

- Cellulose fiber.
- Glass or quartz fiber.
- Mixed fiber filters (glass, cellulose, asbestos, etc.)

- Membrane filters (cellulose esters, Teflon, Nylon, etc.)
- Nucleopore filters.

Cellulose fiber filters do not have uniform pore sizes and tend to have unpredictable collection efficiencies for fine particles; however, they have high mechanical strength and are inexpensive. For air sampling, Whatman No. 41 is a commonly used cellulose filter. Glass or quartz fiber filters have the advantages of withstanding higher temperature, having reduced hygroscopicity, and yielding better collection efficiencies. They are used extensively in high volume samplers. Disadvantages of glass and quartz filters, compared to cellulose filters, include reduced mechanical strength due to fragility, adsorptive loss of organics, and cost. Mixed fiber filters are used primarily for air cleaning, due to their high collection efficiency. They are typically not used for analysis because of the difficulty associated with complete recovery of samples for analysis. They can be appropriate for gravimetric methods not requiring separation of sample from the filter, as well as for collection of radioactive particles for analysis. Membrane and nucleopore filters have a well defined pore size distribution and have very predictable sampling properties. However, these filters are expensive, have a relatively high resistance to flow, and have a rather low sampling capacity. Many membrane filters are soluble in organic solvents, which could be an advantage or disadvantage in recovery, depending on the analytes of interest.

4.3.2. Centrifugal Collection and Impaction

Most particle sampling approaches other than filtration are employed for the purpose of size classification of particulate matter. The primary reason for collecting size fractionated particle samples is to distinguish respirable particles (<10 um diameter) from larger particles. Although the most common objective is to compare particle mass in each size range, the chemical composition is of interest in certain cases. Methods for collecting size fractionated particulate samples generally rely on the difference in momentum (mass times velocity) of the various size particles. Devices operating on this principle include cyclones (centrifugal collectors) and impactors. Both of these devices collect particles of a specific size range, based on the design of the apparatus. Cyclones tend to have a rather broad size cut, whereas impactors have a much sharper size cut. These devices are useful for particles greater than approximately 1 um in diameter and are often used as the basis for "respirable" particle determinations.

A device has been developed by EPA for sampling large volumes of size fractionated ambient particulate matter (51). This device called the "Megavolume Respirable Particulate Sampler" consists of a cascade impactor followed by an electrostatic precipitator. The absence of a filter reduces the pressure drop and allows higher sample flow rates (up to 15 m^3/minute). Particles of greater than 20 um and <1.7 um are collected. This device has the disadvantage of being very bulky (4 ft x 2 ft x 2 ft), and the effect of electrostatic precipitation on chemical composition has not been thoroughly investigated.

4.3.3. Electrostatic Precipitation

Electrostatic precipitation (ESP) method is capable of capturing particles greater than 0.1 mm and serves as an alternative to filtration for the collection of fine particles. A high electrical field (12-45 kv) is maintained between a series of parallel plates. Particles entering the field become charged by ions present in the gas phase and are attracted to the plates.

This sampling, compared to filtration, approach allows large sample volumes to be collected, due to the lower pressure drop. However, the effect of the corona discharge and associated reactive species (e.g. ozone) generated in the ESP on organic chemical composition is of concern and has not been thoroughly investigated. Removal of collected particles from the electrodes is accomplished by rapping or vibration, which seldom results in quantitative recovery. For these reasons, collection of particulate matter for trace analysis of toxic organic constituents by ESP should be thoroughly compared with other available methods of collection.

4.4. GAS AND SOLID PHASE DISTRIBUTION ANALYSIS

Recently much attention and work has been focused on investigating the distribution of semi-volatile organic compounds (PAH, PCB, pesticides, etc.) between the vapor phase and the particle-bound, condensed phase as they exist at ambient conditions. The knowledge of gas and solid phase distribution of air pollutant is important for understanding atmospheric transport, residence time, and fate of these air toxics, as well as in development of sampling methods and designing pollution control systems. Conventional filter and adsorbent backup traps have been subjected to volatilization transfers and are believed to yield erroneous data concerning phase distribution. Denuder-based gas/particle sampling systems have been designed and evaluated for more effective collection of vapor/solid distributed compounds in air. The denuder sampling system is similar to the standard EPA PS-1 sampler with the incorporation of a multiple tube denuder ahead of the filter.

Field evaluations of a denuder sampler in conjunction with a PS-1 sampler yield total concentration, fractional phase distribution, and artifact formation data for target compounds (52). The first results of field investigation representing direct phase distribution measurements on SVOC's conducted by EMSL/RTP and Battelle Columbus Division demonstrated the possibility of separate collection of both gas and solid phases with a denuder sampler, while maintaining data integrity. However, the system used was a low-volume sampler sensitive only to major PAH compounds in air. Subsequently, a compact, high volume multiple annular denuder sampler has been designed and laboratory tested to yield 95% vapor removal efficiency and operating flow rates up to 200 L/min with no measurable loss of particle transmission. It also has direct thermal recovery potential. Two such systems are under development and evaluation (53).

An experimental system for investigating vapor-particle partitioning of trace organic pollutants has been designed utilizing a stainless steel mixing chamber to generate vapor-phase SVOC under high-volume sampling conditions (54). Vapor-particle (V/P) distribution for selected compounds are estimated in the laboratory using the apparent partition coefficient A[TSP]/F, where A and F are the adsorbent and filter-retained concentration (ng/m^3) and [TSP] is the total suspended particle concentration (mg/m^3).

SECTION 5

OVERVIEW OF ANALYTICAL METHODS

This section presents a general description of some analytical methods used in determining ambient atmospheric concentrations of organic compounds. The first subsection discusses physical and chemical properties of concern that govern the applicability of various analytical techniques. The next subsection presents field screening techniques, which are relatively inexpensive and are rapidly performed in the field. The third subsection covers laboratory screening techniques that are more precise at identifying classes of compounds based on functional groups present. In the final subsection compound specific methods such as gas chromatography (GC), high performance liquid chromatography (HPLC), and mass spectrometry (MS) techniques are presented. No one analytical technique will be ideal for all organic compounds, and thorough consideration of the species of interest and program objectives should be conducted before applying any approach. Section 6 provides more detailed, specific applications for particular organic compounds of interest.

5.1. CHEMICAL AND PHYSICAL PROPERTIES

In many respects the chemical and physical properties of concern in sampling method selection are of similar importance in the selection of analytical methods. However, important differences in emphasis exist and must be recognized. Properties of primary concern include:

- Physical state (gaseous or adsorbed)
- Volatility
- Polarity
- Solubility
- Ionic character
- Reactivity
- Thermal stability
- Chemical composition

One of the most important properties governing the selection of analytical methods is volatility. Sample preparation procedures, whereby the analytes of interest are delivered from the sample matrix into a form suitable for analysis, generally involve either solvent extraction/concentration or thermal desorption/cold trapping approaches. Highly volatile compounds (e.g. boiling points below 100° C) cannot be readily analyzed by solvent extraction/concentration approaches because of losses during the concentration process and interference from the solvent to the analytical system. On the other hand, compounds with boiling points above 250° C usually are not candidates for the thermal desorption approach.

Volatility, polarity, and thermal stability must also be considered in the selection of determinative techniques, because gas chromatographic (GC) procedures are not suitable for non-volatile, highly polar, or thermally labile compounds unless special precautions are taken. Generally, polarity and thermal stability are limiting factors for GC determination of organic compounds in ambient air, since these compounds tend to be sufficiently volatile.

Ionic character, water solubility, and reactivity are primarily of concern during sample preparation procedures involving liquid extraction or adsorption chromatography and for determinative procedures such as high performance liquid chromatography (HPLC). Ionizable compounds (acids or bases) require careful control of pH when aqueous systems are employed.

Generally, ionizable compounds are converted to their nonionized forms by adjusting the pH two to three units below the pKa for acidic compounds and two to three units above the pKb for basic compounds. Highly reactive compounds may present problems in the sample preparation procedure through reaction with solvents or adsorption chromatography supports. Phosgene, for example, reacts readily with water; thus water must be carefully excluded from the sample preparation scheme.

Chemical composition is important in the selection of determinative techniques. Whenever possible, a selective detection system for the compound class should be used. Suitable selective detection systems for GC analysis are available for halogens, as well as nitrogen-, sulfur-, and phosphorous-containing compounds. HPLC analysis is appropriate if UV absorbing (usually aromatic), fluorescent, or electrochemically active (e.g. phenol, aromatic amines) functional groups are present in the molecule.

The chemical and physical properties of major compounds (other than those of interest) present in the sample should be considered, since these compounds represent potential interferences. Whenever possible, analytical and sampling techniques should take advantage of differences in properties between compounds of interest and other compounds, to minimize interference in the methods.

5.2. FIELD SCREENING TECHNIQUES

The term "screening technique" can imply different approaches to different people, and therefore an introductory definition is necessary. In this document "field screening techniques" will refer to techniques which can be accomplished rapidly and with relatively inexpensive instrumentation in the field. This definition excludes sampling and analysis approaches which involve conventional sampling techniques and subsequent application of group specific methods in the laboratory. This definition also excludes devices such as mobile mass spectrometers (MS) and triple quadrupole MS/MS systems because these systems are relatively expensive.

This limited definition for "screening technique" should not be viewed as an implication that the excluded sampling and analysis approaches are not useful. Indeed, many circumstances arise where such techniques are extremely useful and should be employed in preference to (or in addition to) the other techniques described in this document. The purpose in limiting the definition of "screening technique" in this way is to present a discussion of alternative approaches which can be used to evaluate whether or not TOAPs are present at a particular site. This evaluation should be accomplished rapidly (e.g. be field operable) and with a minimum of expense (since a multitude of sites may need to be investigated). Such techniques need not be selective for a particular compound but should be capable of distinguishing organic components (e.g. methane) typically found in uncontaminated air from hazardous substances (e.g. chlorinated and aromatic hydrocarbons). If possible, the technique should indicate the class of organic compound present so that subsequent detailed investigations of a site can be directed toward a limited set of target compounds, thereby minimizing the cost and time associated with detailed investigations.

For the purpose of this document the available screening approaches can be broadly subdivided into the following subsections:

- Colorimetric methods.
- Spectroscopic devices.
- Ionization devices (with or without gas chromatographic separation).
- Photometric devices (with or without gas chromatographic separation).
- Passive monitors or dosimeters.

One must be aware that most screening devices have been designed to meet monitoring needs of the industrial hygiene community, among whom part per million levels are usually of concern. Consequently, if one must detect part per billion levels in ambient air, many of these devices will not be sufficiently sensitive.

In the following subsections the operating principles, advantages, and limitations of the various screening approaches are discussed.

5.2.1. Colorimetric Detection

Colorimetric devices involve drawing the air sample through an adsorbent or solution containing a reagent which reacts with the compound(s) of interest to yield a colored material. The degree of color change is proportional to the concentration of the adsorbed analyte. The specificity of such methods is highly dependent on the compound being monitored, and one must be cognizant of the fact that some airborne components may create a positive or negative interference in the method. Humidity, temperature, and sample flow rate can affect the results obtained, and consequently these variables must be known and controlled whenever possible.

The most common type of colorimetric device use for air monitoring is the gas detection tube. Tubes of this type are available for long-term, time weighted average exposure and short-term grab sampling. These tubes are also used extensively for personal exposure monitoring. Some sample passively and can be worn on the outer clothing of workers. Others draw a precise sample with the use of a hand-held volumetric pump attached to the tube.

The concentration of the substance being monitored is determined by one of two methods: In one system the entire tube changes color; the extent of color change is then compared to a standard color chart. The second method draws the sample into the tube, and the reagent stains over a segment of the length of the tube. The length of the stain is concentration dependent. Tubes of this type have calibrated scale markings for direct measurement recording.

The procedures for use are fairly simple, and manufacturers provide detailed information on the specifics of the reactions involved. Tubes are refrigerated until use, then allowed to reach ambient temperature. Reagent expiration dates should be observed, and a system leak check performed before sampling.

Detection limits for organic compounds being tested in the detector tube are generally 0.1 ppmv or higher and often will not be adequate for monitoring ambient levels directly. However, this level of sensitivity may be sufficient for monitoring air in the vicinity of hazardous waste dumps, chemical spill sites, and similar sources where a rapid, inexpensive, qualitative assessment is desirable.

Colorimetric devices other than gas detection tubes are available. One such device uses an integrated liquid pumping system to trap the component of interest, react it with a color developing reagent, and measure the absorbance continuously. This device, while suffering from the same sensitivity and selectivity limitations as the detector tube, offers a continuous monitoring capability which can be useful for rapidly surveying an area for sources of contamination. Currently, this device can detect formaldehyde, acrylonitrile, and a variety of inorganic species with detection limits of 0.05 to 0.5 ppmv. However, this basic system could conceivably be applicable to many more compounds, by using alternate color developing reagents.

Another colorimetric approach involves impregnating a continuous paper tape reel with a color reagent and passing air through the tape. The tape is slowly driven from the air sampling region to an optical detector which measures the absorbency at a specified wavelength. Currently, devices for the detection of isocyanates, dinitrotoluene, phosgene, and a variety of inorganic species are available. Detection limits of a few ppbv are achievable for selected compounds (e.g. toluene, diisocyanate), although the detection limits and selectivity of this approach are generally similar to the other colorimetric approaches. Nevertheless, this approach can be used for continual area monitoring to observe temporal changes in concentration of selected components.

5.2.2. Spectroscopic Devices

Although a wide variety of spectroscopic techniques (e.g. infrared spectroscopy [IR], ultraviolet adsorption [UV], fluorescence, etc.) could potentially be applied to air monitoring, only IR has been employed to a significant extent. UV spectroscopy is too nonspecific to be of any real value, and fluorescence detection is applicable only to a few selected compounds, although either of these techniques could be useful in selected cases.

Infrared spectroscopy is a powerful analytical tool because of its specificity, sensitivity, versatility, speed, and simplicity. Because every compound has its own individual characteristic spectra, quantitative and qualitative identification of compounds and compound classes based on adsorption bands exhibited by their functional groups can be accomplished. Analysis of integrated samples as well as continuous monitoring can be performed. Several variable wavelength and path length IR spectrophotometers are available for both field and laboratory use. Analytical parameters (reference and analysis filter wavelength) for monitoring approximately 100 organic compounds are available. IR spectra libraries are available for several thousand organic compounds.

Major limitations of the IR method are: (1) many inorganic gases (e.g. H_2O, CO, NO, etc.) are also absorbed at wavelength that may interfere with analysis; (2) IR absorbance is not as strong as UV absorbance, hence the poor detection limits (1-10 ppmv). The latter are minimized by employing long, folded-path optical cells (20 meters). Microcomputer control of commercial IR screening devices has partially overcome the first limitation by allowing automated correction for interference. Drying tubes, ascarite traps, and the use of zero gas also reduce interference from moisture, carbon dioxide, and other inorganic gases present in ambient air.

5.2.3. Ionization Devices

Ionization techniques operate on the principle of subjecting the analyte to a high energy source, with subsequent detection of the ionized species by collection at an appropriate polarized electrode. The most widely used applications of this type are (a) flame ionization detection (FID), (b) photoionization detection (PID), and (c) electron capture detection (ECD). Each of these can be used in a "stand alone" mode for total organic measurements or can be coupled with a gas chromatograph to provide greater specificity.

Flame ionization detection (FID) - As its name implies, FID involves the ionization of organic components of the atmosphere in a flame. A hydrogen/air flame is used because the concentrations of ions within it are low. The FID responds to virtually all organic compounds, that is, compounds which contain carbon-hydrogen or carbon-carbon bonds. The introduction of organic compounds into the flame results in formation of ions, which reduces the electrical resistance of the flame. This change in resistance is detected by electrodes and is proportional to the hydrocarbon concentration. Flame ionization detectors are used in most of the commercially available "total hydrocarbon" and "non-methane hydrocarbon" analyzers. Typical detection limits for such devices are about 0.5 ppmv (as carbon). Another appealing feature of FID is its wide range of linearity. A description of sensitivity variations of two commercial FID's has been presented (52).

In addition to the commercially available total hydrocarbon monitors, several portable GC/FID systems are available. These GC/FID systems provide qualitative as well as quantitative field analysis. When coupled with a GC, FID effectively identifies specific compounds of interest which are separated on the GC column from methane and other ubiquitous organic compounds.

In addition some of these GC systems can utilize alternate detectors to provide even greater qualitative information, as well as better sensitivity for selected groups of compounds.

Photoionization detection (PID) - can be used to measure a wide range of toxic compounds. PID involves subjecting the gas phase compounds to a high-intensity beam of UV radiation of a particular energy. Excitation of the gas molecule by UV energy results in the formation of a positive ion and a free electron. The degree of ionization is dependent upon the ionization potential characteristic for each compound. The ions are collected on positive and negative electrodes, resulting in a flow of current proportional to the concentration of the ionized species. The convenience of this method is the fact that natural components of ambient air (oxygen, nitrogen, carbon dioxide, and water) have much higher ionization potentials and are thus not detected.

Because the ionization potential of a particular compound must be less than the radiation energy, compounds having high ionization potentials will be less easily detected than those compounds of lower ones Consequently, the choice of lamp energy will have a profound effect on detector specificity. This aspect of PID detection is attractive from the standpoint that use of a higher energy lamp will provide a relatively nonselective, less sensitive detector, whereas a lower energy lamp will yield a selective detector which can sensitively detect certain readily ionized compounds (e.g. aromatic hydrocarbons) but will not detect aliphatic hydrocarbons. While more species can be detected with high energy lamps, the reduced life expectancy and lowered sensitivity limit their usefulness.

Several PID devices and a variety of lamp energies ranging from 9.5 to 11.7 eV are available. In general, the ionization potential for important groups of organic compounds increases in this order: aromatics <olefins<halogenated hydrocarbons<aliphatic hydrocarbons. Consequently, aromatics can be selectively detected in the presence of halogenated alkanes, for example, using a low-energy lamp (e.g. 9.5 eV), whereas both compound classes can be detected with an 11 eV lamp. An important advantage of the PID system is that methane is not detected by the use of any of the available lamps and hence does not interfere.

The sensitivity of PID is considerably greater (100 ppbv or better) than that of FID, and several manufacturers produce field-portable GC/PID systems. These devices have advantages similar to the GC/FID system, in that qualitative as well as quantitative data are obtained. However, while the PID system is generally more sensitive than FID, the PID system does not give uniform response from compound to compound. Hence, the system must be calibrated for each specific analyte in order to yield quantitative data.

Electron capture detection (ECD) - In this technique the gas sample is introduced into an electron cloud produced by a radioactive source (usually from ^{3}H or ^{63}Ni). When an electron-capturing species (such as halogenated or nitrogenated organic compounds) is subject to an electron source, a decrease in the standing current gives a response which is a measurement of the analyte's concentration and electron capturing efficiency. Unfortunately, response varies widely from compound to compound and requires specific calibration for every compound analyzed. The detector can be calibrated at standard atmospheres of the material to be monitored and has a detection sensitivity of about 10 pg.

ECD's can be used for leak seeking of trace organics and provide adequate quantitative data. Instruments are used for continuous monitoring and are also coupled with gas chromatography. "Stand alone" ECD detectors are not as applicable in selecting organics as FID and PID. They are also sensitive to inorganic gases and particles and can only be used in a controlled gas stream using N_2 or argon/methane gas carriers. Response time for ECD is about one second for continuous monitoring and fifteen seconds for column types. At least one portable GC/ECD is available and is selective for halogenated organics such as carbon tetrachloride and trichlorethylene and for nitrogen derivatives. When using the ECD technique, care should be taken not to overexpose a particular compound to the detector, as it will become saturated and take some time to recover.

ECD detectors are moisture sensitive, and some type of preconcentration is recommended for removal of moisture from the sample. ECD's are also a source of radiation and must be registered accordingly, a consideration that may impact purchasing such a device.

Solid state detectors and semiconductors - Another technique applicable to measuring pollutants has been the use of two types of solid state detectors: One type measures the heat of reaction produced by oxidation of a gas on the surface of a catalytic solid. The second measures change in electrical conductivity of a semiconductor, when interacted with ionic species.

Pellistor detectors, of the first class, were originally developed for measuring explosive levels of volatile gases and have limited applications for detecting trace level toxic organic compounds. Semiconductor devices measure conductivity changes associated with oxidation and reduction reactions on the surface of the semiconductor made of oxides of heavy and transition metals. Many instruments use semiconductors and solid state devices which measure a wide range of toxics with sensitivity ranges from 1 ppm upward.

5.2.4. Photometric Devices

Photometric techniques involve monitoring radiant energy emitted by a species subjected to physical or chemical excitation processes. The two most common techniques in this category are flame photometric detection (FPD) and chemiluminescence.

Flame photometric detection (FPD) is based on a spectroscopic principle which certain elements exhibit when introduced into a hydrogen/air flame. The light emitted by such elements (e.g. sulfur and phosphorus) is intensified in emission bands of a particular wavelength which can be monitored and quantified. The element to be monitored is selected by placing an appropriate optical filter in front of a photomultiplier tube to allow only light of the wavelength of interest to be detected. For example, sulfur compounds are detected using an optical filter selective for the wavelength of 394 nm. While several elements could be monitored by this approach, generally only sulfur and phosphorus compounds are analyzed.

The FPD is used as a total sulfur or phosphorus detector in a "stand alone" mode (similar to FID for total hydrocarbons). However, inorganic as well as organic species will be detected, and common inorganic gases such as SO_2 will interfere with organic analysis. Consequently, use of GC/FPD is advantageous for monitoring sulfur or phosphorus-containing organics. Detection limits of 10 to 100 ppbv (as S or P) are achievable in many cases. Detector response is nonlinear.

Chemiluminescence involves the measurement of light emitted from a compound which has been activated by a chemical process. The only chemiluminescent process to be discussed here is the detection of nitrogen compounds by conversion of the compound to NO and subsequent reaction with ozone. The chemical reactions involved are as follows:

$$\mathrm{R\text{-}N + O_2 \xrightarrow{\text{(pyrolysis)}} CO_2 + H_2O + NO}$$

$$\mathrm{NO + O_3 \longrightarrow NO_2^{*} + O_2}$$

$$\mathrm{NO_2^{*} \longrightarrow NO_2 + light}$$

While this approach is highly selective for nitrogen, it does not distinguish between inorganic and organic nitrogen and thus cannot be used to detect trace quantities of organic nitrogen compounds in air. Commercially available systems involving GC preparation have been developed. This technique for determining trace organic nitrogen compounds in air provides a method for removing the NO_x and other inorganic nitrogen compounds.

5.2.5. Summary

While a large number of screening devices and techniques are available, one must carefully evaluate the sensitivity, selectivity, and types of interferences of these techniques before deciding whether or not they are suitable for use in a particular monitoring situation. Many of the available techniques are designed for workplace monitoring where the levels of interest are greater and the environment is better known and controlled than is generally the case for ambient air monitoring.

In many cases none of the available screening techniques will be suitable to accomplish a given monitoring objective; therefore, a more sophisticated analytical approach will be required. In selected cases the existing screening devices may be suitable if some means of sample pre-concentration or cleanup is employed. However, extensive sample workup in the field is generally cumbersome and probably offers little advantage over conventional laboratory analysis of the sample.

The ionization devices (particularly FID and PID) probably are the most generally useful in terms of sensitivity for ambient air monitoring, although colorimetric methods can be quite effective in favorable cases. A further advantage of the ionization and photometric approaches is the availability of these techniques in combination with gas chromatography, which extends the qualitative as well as quantitative capabilities of the techniques. The IR spectroscopic approach can give useful qualitative information unavailable by the other techniques but will not be useful for monitoring ambient levels of many trace components because of spectral overlap from major organic and inorganic components. The lack of suitable GC/IR for field use is a further limitation of this approach.

5.3. LABORATORY SCREENING TECHNIQUES

Laboratory screening techniques generally require the use of more sophisticated techniques than are applied under field conditions.

The techniques discussed in this section primarily give compound class information, rather than data for specific compounds. Many techniques discussed in the preceding section fit this description, although the current discussion centers on techniques primarily designed for laboratory rather than field use.

Techniques applicable in this category include:

- Colorimetric techniques.
- Infrared spectroscopy.
- Fluorescence spectroscopy.
- Low resolution mass spectrometry.

Some of these techniques can be used to obtain compound class information, as well as to determine concentrations of specific compounds. Compound specific methods based on these techniques are discussed in Section 6. The techniques themselves are described below:

5.3.1. Colorimetric Techniques

A variety of available colorimetric techniques have application to the analysis of TOAP's. Colorimetric techniques exist for aldehydes, mercaptans, phenols, amines, and polynuclear aromatic hydrocarbons and in some cases have been incorporated into Toxic Organic Methodology (TO-5, TO-6, TO-8, and TO-11). Relatively few compound class methods for ambient air have been developed in the last few years because of the advances in chromatographic procedures and the intense interest in determining specific organic compounds.

Most colorimetric techniques involve collection of the compound(s) of interest in an impinger in either the field or the laboratory, with subsequent formation of a colored derivative. The content of the impinger solution should be chosen to (a) stabilize the analytes during collection and transport and (b) selectively capture the analytes of interest, allowing potential interferents to pass through.

5.3.2. Infrared Spectroscopy (IR)

IR is widely used as a screening tool for determining organic compound classes from source emissions in the EPA Level 1 protocol (55). However, this approach is generally less sensitive than available colorimetric approaches and will be of value in ambient air monitoring only when high (ppm) levels of semi-volatile or nonvolatile compounds are present.

The Level 1 IR approach cannot be used for volatile compounds (boiling point less than 100°C) because of the need for solvent extraction. Gas phase IR approaches such as those described for field screening could be employed in the laboratory, but the problems associated with sample transport make this approach less attractive. Long path IR approaches for determining specific organic compounds are discussed later.

5.3.3. Fluorescence Spectroscopy

Fluorescence is a relatively inexpensive and highly sensitive technique useful for determining selected classes of organic compounds. The principle of fluorescence spectroscopy, as applied to air monitoring, is discussed in Katz's book (56). Polynuclear aromatic hydrocarbons (PAH), aromatic amines, and phenols are the primary classes of organic comounds in ambient air which can be determined using fluorescence spectroscopy.

A practical limitation of fluorescence spectroscopy is the quenching phenomenon, whereby large quantities of UV absorbing material reduce the fluorescence response. Consequently, large quantities of UV absorbing material must be removed from the sample extract (e.g. by adsorption chromatography) before a fluorescence determination can be made. A second limitation is the wide variability in fluorescence response from compound to compound, even within a given class. This limitation makes development of a quantitative fluorescence method for compound classes difficult. As a result of these two limitations most available fluorescence methods involve chromatographic isolation of a particular compound, prior to its determination.

5.3.4. Low Resolution Mass Spectrometry (LRMS)

LRMS is another technique used in the EPA level 1 protocol (55). This approach suffers from the same limitations as IR when applied to ambient air monitoring. While the LRMS approach is somewhat more sensitive than

IR, the data obtained are more difficult to interpret, and the instrumentation required is more sophisticated and expensive. Consequently, this approach is of little value for ambient air monitoring.

5.4. COMPOUND SPECIFIC TECHNIQUES

A listing of available techniques for determining specific organic compounds is given below:

- Gas chromatography (GC).
- Gas chromatography-mass spectrometry (GC-MS).
- High performance liquid chromatography (HPLC).
- Thin layer chromatography (TLC).
- Column chromatography.
- Infrared spectroscopy (IR).
- Ultraviolet or visible absorption (UV-VIS).
- Fluorescence spectroscopy.

Operating principles as well as advantages and limitations of the various techniques are discussed in the following subsections.

5.4.1. Gas Chromatography (GC)

GC is by far the most widely employed technique in ambient air monitoring of toxic organic compounds. The sensitivity, specificity, and versatility of GC, coupled with the relatively volatile nature of most compounds in ambient air, make this a very attractive technique.

The following discussion of GC principles is designed to present those aspects of GC operations important to ambient air analysis. Although the operation of GC is rather simple, many practical problems can arise which can be avoided or corrected only by experienced operators. Consequently, the availability of such personnel is essential to the success of a monitoring program. It must be remembered that a large number of compounds may be detected by gas chromatography, even when using specific detectors and special columns. Coelution can be a problem if adequate consideration of sample composition is not given when columns are selected. Great care must be exercised to ensure that reported results are accurate, since much of the need for toxic organics monitoring exists in environments where a wide range of potential contaminants may occur.

Basically, GC is a separation technique wherein components of a sample are separated by differential distribution between a gaseous mobile phase (usually helium, nitrogen, or hydrogen carrier gas) and a solid or liquid stationary phase held in a glass or metal column. The sample is injected into the carrier gas as a sharp plug, and individual components are detected as they elute from the column at characteristic "retention times" after injection. Both column temperature and carrier gas flow must be carefully controlled to obtain uniform response and retention time characteristics. The basic components of a gas chromatograph are:

- Gas flow system.
- Injector system.
- Stationary phase (column).
- Oven and associated temperature controller.
- Detector.
- Data recording device.

Only columns, detectors, and injectors will be discussed in detail.

5.4.1.1. Column Types

In order to understand the requirements for the various GC components, one must recognize that two different types of GC columns are widely used. The conventional type is called a "packed column" and consists of a solid support coated with a liquid stationary phase (gas/liquid chromatograph) or simply a solid adsorbent (gas/solid chromatography). The second type of column is a wall-coated open tubular (WCOT) or capillary column and has been widely adopted for environmental analysis because of its superior resolution and broader applicability, compared to packed column GC. The capillary column consists of a liquid stationary phase coated or bonded to specially treated glass or fused silica tubing. Fused silica tubing is most commonly used because of its physical durability and superior inertness. Bonded (or cross-linked) columns are used in preference to coated columns because of the greater operating temperatures which can be obtained. A significant advancement in column technology is the development of wide-bore capillary columns. These columns can be loaded at rates equivalent to packed columns, yet offer the resolution available with capillary columns. The principles and applications of capillary column GC are discussed in the appropriate literature (58,59).

The typical linear flow velocity through both capillary and packed columns is about 30 cm/sec. However, the much narrower cross sectional area of the capillary column (0.20 to 0.32 mm ID) translates to a volumetric flow rate of 1-2 cm^3/minute versus 30-50 cm^3/minute for the packed column. The lower flow rates of capillary columns require that dead volume in the injector and detector be minimized and that the effective sample injection volume be reduced. These requirements have been fulfilled satisfactorily in most modern GC instruments through the use of low volume detector cells and split/splitless-type injection systems. These columns provide superior resolution of complex samples when the method of sample introduction is a concentrated liquid extract. However, the low volumetric flow rate and limited capacity for absorption of analytes present some problems in the use of these columns.

Recent advances in capillary column technology have produced wide bore and ultrawide bore capillary columns with ID's of up to 0.75 mm. These columns are particularly well-suited to air sample analysis using various injection techniques. The columns can operate at higher flow rates, up to about 20 mL/minute. Larger sample volumes can be injected by gas sampling loops or syringes, without producing severe peak broadening of the early eluting compounds. It should be noted that resolution of C_1 through C_3 substituted aromatics using capillary column technology is very difficult.

While the use of packed columns has decreased in recent years, these columns are still very effective for many analyses. The very low boiling compounds, such as methane, chloromethane, ethylene, and others are difficult to resolve using capillary column techniques, unless cooling the compounds to subambient temperatures is possible. Packed columns using carbon molecular sieves are very effective for performing this type of analysis. Also, the stationary phase selection available on packed columns far exceeds that for capillaries.

5.4.1.2. Detector Types

The GC detection system chosen determines, to a large extent, the specificity and sensitivity of an analytical method. Consequently, one should carefully review the program requirements when selecting a detection system for use in a given study.

The primary detector types in use today are:

- Flame Ionization Detector (FID).
- Electron Capture Detector (ECD).
- Photoionization Detector (PID).
- Flame Photometric Detector (FPD).
- Alkali Bead Thermionic Detector.
- Hall Electrolytic Conductivity Detector (HECD).
- Mass Selective Detector (MSD).
- Chemiluminescence Detector (CLD).
- Fourier Transform Infrared Detector (FTIRD).

Table 5.1 provides an overview of the characteristics of available detection systems. The principles of operation for many detectors are briefly described in the section on field monitoring techniques.

TABLE 5.1

COMMONLY USED GC DETECTORS

Detector	Compounds Detected	Advantages	Limitations
Flame Ionization (FID)	Organics	Response is a relative constant from one compound to another.	Not as sensitive as many other detectors.
Photoionization (PID)	Most organics except methane	Response selectivity can be varied by choice of lamp energy.	Response varies from compound to compound. Less rugged than FID.
Electron Capture (ECD)	Polyhalogenated and nitro compounds	Highly sensitive and selective.	Subject to contamination. Response varies widely from compound to compound. Response drifts during temperature programming. Oxygen in air may cause analytical difficulties when direct injection is used.
Alkali Flame (NPD or AFD)	Nitrogen and phosphorus compounds	Highly sensitive and selective.	Subject to contamination. Response varies more from day to day than for FID or ECD.
Fourier Transform Infrared Spectroscopy (FTIR)	Most organics	May be highly sensitive, using long path length cells. Highly selective.	Primarily a laboratory instrument. Very expensive
Flame Photometric Detector (FPD)	Sulfur or phosphorus compounds (separately)	Highly selective.	Response varies from day to day. Not as sensitive as NPD for phosphorus compounds.
Hall Electrolytic Conductivity (HECD)	Halogen, sulfur, or nitrogen compounds (separately)	Highly selective. Response relatively constant from compound to compound. Stable base line during temperature programming.	Only halogen mode has been employed extensively. Requires considerable operator attention. Not as sensitive as ECD for polyhalogenated compounds (e.g. PCB's).
Thermal Energy Analyzer (TEA)	Nitrosamines	Highly sensitive and selective.	Very expensive (~$35K)
Mass Selective Detector (MSD)	Most organics and volatile inorganics	Response is very selective and selectable for specific compounds.	Very expensive (~$40K). May only detect a limited number of compounds per sample. Requires a more highly trained operator and more attention. Not usually as sensitive as FID or ECD.
Chemiluminescence Detector (CLD)	Nitrogen compounds	Highly selective and sensitive	Recently developed. Limited data on applications.

By far the most widely used GC detector is the flame ionization detector (FID), which provides good sensitivity and uniform response based on the effective number of carbon atoms for a wide variety of compounds. The uniformity of the FID's response allows fairly accurate quantification of compounds for which specific response factors have not been determined. This is probably the most advantageous feature of the FID and is useful for ambient air monitoring studies in which the complete range of compounds present cannot be anticipated. None of the other detectors gives nearly as uniform a response as FID, for compounds in a given class. Another major advantage of FID is the very wide linear dynamic range of the response. The detector itself is linear over a range from subnanogram to milligram quantities of a detected compound.

The electron capture detector is becoming more widely used in ambient air monitoring because of its greater sensitivity, compared to FID. ECD is selective for electron deficient materials, especially polyhalogenated and nitrosubstituted compounds. In favorable cases, picogram (10^{-12}g) levels can be detected, but response varies widely from one compound to the next. Several literature references which describe the detection sensitivities of various compounds on ECD are available (60-62). A drawback sometimes encountered when using ECD on direct injected gas samples is the quenching effect of oxygen from the air on the detector response. This limitation sometimes precludes use of ECD for certain analyses.

Like ECD the photoionization (PID) detector is enjoying wider use in ambient air monitoring because of its greater sensitivity and selectivity in comparison to FID. PID is widely viewed as a substitute for FID, although its response varies considerably from compound to compound. PID is particularly useful for monitoring aromatic compounds. References describe the detection sensitivities for various compounds of PID (60-62).

The flame photometric (FPD) detector is specific for either phosphorus or sulfur compounds, depending on the optical filter employed, and gives sensitivity comparable to or greater than FID. The response obtained is logarithmically related to the amount of sulfur or phosphorus injected. This detector is of particular advantage when trace levels of phosphorus or sulfur compounds must be detected in the presence of much greater quantities of aliphatic hydrocarbons.

The alkali flame (AFD), thermionic specific (TSD), or nitrogen-phosphorus (NPD) detector is selective for nitrogen and phosphorus compounds and is considerably more sensitive than either FPD or FID. However, response varies considerably from compound to compound. This detector is preferred over FPD for determining phosphorus compounds, in many cases, because of its greater sensitivity.

The Hall electrolytic conductivity detector (HECD) can be operated in either halogen-, sulfur-, or nitrogen-specific modes, although the halogen-specific mode is the most widely employed. This system gives poorer sensitivity than ECD for polyhalogenated compounds but better response for monohalogenated compounds such as vinyl chloride, since the HECD response is proportional to the amount of halogen injected. Correspondingly, the HECD gives a more uniform response for polyhalogenated compounds than ECD. An additional advantage of HECD is its temperature stability, which allows temperature programming (ECD drifts considerably under temperature programmed conditions). HECD is not widely used in air monitoring programs because the greater sensitivity of ECD is highly desirable and tends to outweigh other considerations.

A continuing challenge in GC analysis of organic compounds in ambient air is the qualitative identification of components identified by the various detection systems. Use of mass spectrometry as a GC detector (GC-MS), a highly effective tool in this regard, is discussed later in this section. However, GC-MS is a very expensive instrument and is not always available. A less costly, though still expensive, option is the mass selective detector. This detector is basically a mass spectrometer without full scanning capabilities. The detector can be set up to monitor from three to ten ions selected by the operator. These may be changed during the run. The ions selected are characteristic of one or more compounds of interest. By observing properly selected multiple ions for a single compound, qualitative information can be gained.

Other attractive alternatives to GC-MS include analyzing samples twice, using dissimilar columns or dual (parallel or series) detectors. The latter approach is more attractive because only a single injection of sample is required, and retention times can be accurately matched from the two outputs. If series detectors are employed, the first detector must be sealed, non-destructive towards the sample, and have a low dead volume to reduce peak broadening. On the other hand, parallel detector operation requires a precise stream splitter. Such a system has been described for simultaneous FID/PID detection using capillary columns GC (60).

Some detector combinations found to be most useful in terms of qualitative information are listed in Table 5.2. Note that each detector combination contains one selective (ECD, HCD, or NPD) and one relatively nonselective (PID or FID) detector. This approach allows the selective and sensitive detection of compounds of special interest, as well as the detection of any large, unanticipated components. The ratio of response for a given peak on the two detectors helps confirm the identity of the compound.

The chemiluminescence detector uses oxidation and reduction of nitrogen in compounds to form nitric oxide. The nitric oxide then reacts with ozone in a light-producing reaction. The detector is highly selective and sensitive for nitrogen containing compounds. Application of this detector to environmental analytes is in its early stages, due to the newness of the detector. Ambient air monitoring by CLD should be seen more in the future.

5.4.1.3. Injection Systems

Injection systems are of particular importance in GC analysis of ambient air, because of the wide range of forms in which the sample may be collected. The primary injection modes, based on the manner of sample collection, include:

TABLE 5.2

USEFUL DUAL GC DETECTOR COMBINATIONS

DETECTOR COMBINATION	APPLICATION
ECD-PID (Series)	Volatile Aromatics and Chlorinated Solvents
PID-FID (Series)	Aromatic Hydrocarbons
ECD-FID (Series)	Chlorinated Hydrocarbons
PID-HECD (Series)	Aromatic and Halogenated Volatile Compounds
NPD-FID (Parallel)	Nitrogen or Phosphorous Compounds
FPD-FID (Parallel)	Sulfur Compounds
PID-NPD (Series)	Amines
HECD-FID (Parallel)	Hydrocarbons and Halogenated Hydrocarbons
FTIR-MS (Series)	Hydrocarbons, Aldehydes, and Ketones

- Liquid injection (particulate or resin extract).
- Whole air injection (syringe or valve).
- Thermal desorption.
- Cryogenic trapping of whole air sample.

Liquid and whole air injections are relatively straightforward and employ conventional techniques. In the case of capillary column GC a well-designed splitless injector is required to obtain optimal resolution and prevent solvent tailing. Generally, the capillary column temperature is maintained well below the analyte's elution temperature, in order to reduce peak broadening.

Thermal desorption of resin samples involves (a) heating the resin cartridge to a suitable temperature in an inert gas stream, (b) passing the inert gas stream through a cryogenically cooled trap to condense the desorbed analytes, and (c) flash evaporating the analytes onto a GC column held at low temperature to "focus" the materials at the head of the column. Instrumentation allowing semiautomatic operation of the system is available.

The whole air, cryogenic sampling procedure is similar to the process described above except that thermal desorption of the resin is omitted. As described in the literature (39) a 30-500 ml volume of air is passed through a cryogenically cooled trap (liquid argon), and the condensed material is flash evaporated onto a GC column held at low temperature (e.g. -50°C). In both cases, the desorbed components are separated by temperature programming of the GC column.

Both resin and cryogenic thermal desorption approaches require the use of nonadsorptive stainless steel or Teflon valves and fittings capable of withstanding extreme operating temperatures without leaking or contaminating the system. Capillary columns should be directly coupled to the injection valve by means of Teflon and stainless steel fittings, as opposed to using conventional splitless injectors.

5.4.2. Gas Chromatography-Mass Spectrometry (GC-MS)

In principle, GC-MS can be viewed as another detection mode for gas chromatography. However, in practice GC-MS is a highly sophisticated and powerful technique requiring more specialized skills and detailed knowledge than required for other forms of GC. A detailed discussion of GC-MS theory and practice is beyond the scope of this document. A comprehensive discussion of GC-MS is available in textbook form (63).

Essentially, mass spectra are obtained by bombarding the sample with an electron beam which knocks electrons or negative groups from the molecule, producing excited and reactive species. These species further decompose, producing ionized fragments characteristic of the parent molecule. The ions are accelerated, passed through a magnetic field, and detected by an ionization gauge. Generally, only the singly positively charged ions are detected. The resulting spectral pattern is characteristic of the molecule and can thus be used to identify different chemical species.

5.4.2.1. Instrumentation

In addition to the GC system the major components of a GC-MS system include:

- Interface (between GC column and MS ion source).
- Ion source.
- Mass analyzer.
- Vacuum system(s)
- Data acquisition and instrument control system.

Mass spectrometric analysis involves the following sequential processes:

- Ionization of the sample introduced into the ion source.
- Acceleration of the ions from the ion source into the mass analyzer region.
- Separation of the ions in the mass analyzer region on the basis of the mass to charge (m/e) ratio.
- Detection of the ions at each mass.

In order to minimize ion-molecule reactions and interference from air the ion source, mass analyzer, and ion detector must be maintained at low pressure (10^{-5}mm of Hg or less). Consequently, the high vacuum system is a critical component of the GC-MS system, and air leakage through valves, fittings, and/or flanges is a common problem in GC-MS.

Because a GC operates at ambient pressure and above, whereas the MS must be maintained at low pressure, the GC-MS interface ideally will discard excess carrier gas flow and quantitatively deliver the sample components into the ion source for subsequent determination. Typical GC-MS systems can accept approximately 2-3 ml/minute of gas flow without significant spectral distortion (due to elevated pressure in the MS system). The use of capillary column GC, therefore, allows the entire column effluent to be delivered to the ion source. If fused silica columns are used, the column can actually be placed directly into the entrance of the ion source. However, packed column GC-MS operation, in which column flow rates of 30-50 ml/minute are common, requires the use of membrane or jet separators to remove a large portion of the light carrier gas (usually helium) delivering the majority of the sample to the ion source.

The avoidance of membrane and/or jet separators and associated fittings, in addition to the other inherent advantages of capillary column GC (i.e. better resolution, less irreversible adsorption), make capillary column GC-MS preferable to packed column GC-MS for most environmental applications. In fact many of the newer commercial GC-MS systems are designed primarily for capillary column operations.

Although a wide variety of powerful, specialized forms of MS ionization modes, mass analysis schemes, etc. are available, the majority of ambient air monitoring applications uses electron impact (70 eV) ionization and quadrupole mass analyzers. One must bear in mind that low resolution mass spectral identifications are considered tentative and for litigation purposes high resolution spectral data may be required. A discussion of the various optional approaches is provided in the previously referenced text (63).

GC-MS analysis of complex environmental samples results in the acquisition of much data. A typical capillary column GC-MS run might result in the acquisition of 2000 mass spectra (e.g. one scan per second) over a range of 40-400 atomic mass units and representing 100-200 individual components. Obviously the acquisition and reduction of this volume of data requires experienced personnel and the use of a laboratory computer system operating with a set of sophisticated software. Typical GC-MS systems use laboratory mini-computers with high density magnetic disks for mass storage. Archival storage of data is usually accomplished using 9-track magnetic tape, a more convenient medium than disks for long-term storage.

A new form of mass spectrometry, termed MS-MS or triple quadrupole MS, has recently become available and is receiving much attention (64). This technique involves direct analysis of an atmospheric sample by (a) ionizing the sample components in an atmospheric pressure ion source, (b) separating the ions in the first quadrupole mass analyzer, (c) passing an ion of one specific mass into a second quadrupole containing a collision gas such as argon, and (d) separating the product ions resulting from the ion molecule reaction in (c) by means of a third quadrupole. The use of two mass analyzers in series introduces great selectivity into the analysis, hence eliminating the requirement for GC separation in many cases. In practice the MS-MS approach is highly sophisticated and expensive, thus limiting its availability for most ambient air monitoring programs. MS-MS techniques have been employed for air quality modeling work and for more monitoring ambient dioxin concentrations at remediation sites. However, in selected cases MS-MS may be the only technique capable of detecting trace levels of contamination.

5.4.2.2. Applications

The power of GC-MS analysis has resulted in a wide variety of applications, especially in the environmental area. Reviews (65) and research articles describing these applications are available throughout the scientific literature, and no attempt will be made to summarize that information here.

GC-MS analysis can be used effectively for ambient air monitoring in two generalized operating modes: The first involves surveying collected samples to determine what compounds are present and their approximate concentrations. A typical example of this operating mode is the widely used Tenax resin collection/GC-MS analysis method for ambient air surveys (66). This operating mode takes advantage of the powerful identification capability of GC-MS and is often used in conjunction with other GC detection schemes, wherein the sample components quantified by FID, ECD, etc. are identified by GC-MS.

The second mode of GC-MS operation involves searching a sample for trace levels of specific compound(s) and accurately quantifying this material. This operating mode typically employs a form of GC-MS termed "selected ion monitoring" (SIM) or "multiple ion detection" (MID) whereby only a few selected ions are monitored, rather than scanning a broad mass region, as in the first operating mode. The SIM approach is much more sensitive and accurate than full spectrum scanning approaches.

5.4.3. High Performance Liquid Chromatography (HPLC)

HPLC is a technique designed primarily for the determination of polar and nonvolatile compounds not readily determined by gas chromatography. Consequently, HPLC is not widely used for ambient air monitoring, in which most compounds of interest are relatively volatile. Two specialized cases in which HPLC is useful for ambient air monitoring are:

- Determination of nonvolatile material (e.g. PAH's) in ambient particulate material.
- Determination of reactive components (e.g. aldehydes) by reacting the compounds with a derivatizing reagent.

The theory and application of HPLC have been described in detail in textbook form (67).

The important components of an HPLC system include:

- Pump.
- Injection valve.
- Column.
- Detector.
- Data recording device.

HPLC separation, like GC separation, involves separation of sample components on the basis of the differential distribution between mobile and stationary phases. However, GC separations are performed primarily on the basis of volatility, whereas HPLC separation mechanisms are much more varied and complex. The liquid mobile phase composition has a profound effect on component retention, and a change in mobile phase composition can lead to reversal of the elution order for two components.

The most commonly employed forms of HPLC are (a) normal phase chromatography and (b) reversed phase chromatography. Normal phase HPLC uses a polar stationary phase (e.g. silica gel, alumina) and a relatively nonpolar mobile phase (e.g. hexane, methylene chloride). Separation is based primarily on an adsorption mechanism, with polar components eluting later than on nonpolar components. Reversed phase HPLC was developed later than normal phase HPLC and uses a nonpolar (usually chemically bonded) stationary phase and polar (e.g. water, methanol, acetonitrile) mobile phase. Reversed phase HPLC separates primarily on a partition mechanism, with hydrophilic components eluting earlier than hydrophobic components. At present, reversed phase HPLC is more widely used than normal phase HPLC because of the greater versatility of this technique.

In order to achieve rapid, efficient separation of sample components, HPLC techniques employ microparticulate packing materials, typically spherical materials of 5 um diameter. HPLC requires a pumping system capable of delivering a precise, pulse-free flow (e.g. 1-2 ml/minute) of mobile phase at pressures of up to 400 atmospheres. Obviously, high pressure injection valves, columns, and fittings are also required. Because of the relatively low flow rates involved (compared to GC) "dead volume" in fittings, injection valves, and detector cells must be minimized to maintain good separation efficiency.

Recent advances in HPLC column technology have resulted in the development of capillary HPLC columns. These columns have the potential to have a similar impact on the HPLC technique that capillary columns had on GC.

A variety of detection systems are available for HPLC. The readily available detectors of value in ambient air monitoring are listed in Table 5.3. By far the most widely used HPLC detector is the UV detector (either fixed or variable wavelength). Unfortunately no sensitive, universal detector (equivalent to GC/FID) is available for HPLC. This limitation tends to reduce HPLC to the role of a specialized analytical tool for determining selected classes of compounds, at least in the ambient air monitoring area. LC-MS technology has advanced to the point where it is technically and practically feasible for confirmatory analysis in much the same fashion that GC-MS is.

5.4.4. Thin Layer and Column Chromatography

Column chromatography and thin layer chromatography (TLC) are widely used as "cleanup" techniques, prior to GC-MS, GC, or HPLC determination, and are no longer widely used as determinative techniques in ambient air monitoring. The few methods whereby these techniques have been used for compound determination, such as PAH analysis (68), have been largely replaced by HPLC methods. However, in some cases (e.g. benzo(a)pyrene analysis in ambient air) TLC has remained a viable technique because of its lower cost compared to HPLC. Both TLC and column chromatography are forms of adsorption chromatography.

5.4.5. Spectroscopic Techniques

Spectroscopic techniques of potential value for compound specific analysis include infrared spectroscopy (IR), fluorescence spectroscopy, and ultraviolet-visible absorption (UV-VIS) spectroscopy. However, UV-VIS and fluorescence spectroscopy are not sufficiently selective to be of value except in combination with chromatographic procedures. Consequently, these two techniques are used as online HPLC detectors as well as offline determinative procedures in combination with GC, TLC, or HPLC. PAH methods using these approaches have been described (70).

TABLE 5.3

HPLC DETECTORS

DETECTOR	APPROXIMATE SENSITIVITY, AMOUNT INJECTED	APPLICATION
Ultraviolet, Fixed, or Variable Wavelength	10^{-9}g	PAH, phenols, nitrogen heterocycles
Fluorescence	10^{-12}g	PAH, aromatic amines, phenols
Electrochemical	10^{-11}g	Aromatic amines, phenols
Refractive Index	10^{-6}g	Too insensitive for environmental applications
Mass Spectrometer	10^{-8}g	Confirmatory analysis for selected organic compounds

IR is also useful as an online or offline determinative tool. The advent of rapid scanning Fourier transform IR (FTIR) techniques has improved instrumental sensitivity and analysis speed, making online GC/FTIR techniques feasible (71). GC/FTIR is still in the early stages, and many commercial instruments are available. Long path (kilometer) FTIR techniques have been used to detect individual compounds (for example, formaldehyde) in ambient air (72). This technique has the advantage that sample collection is not required. However, this is not a readily available technique and hence is of limited value in ambient air monitoring programs.

SECTION 6

SPECIFIC SAMPLING AND ANALYTICAL METHODS

Since the original publication of the TAD, EPA has concentrated on compiling reference methods for the sampling and analysis of toxic organic air pollutants (TOAP's). These efforts have culminated in the publication of a document entitled "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air." Supplements to this document have been published, and additional supplements are expected as new methods become available. Table 6.1 summarizes the various methods currently published in the compendium. These methods represent compatible combinations of the sampling and analytical procedures described in Sections 4 and 5 of this document. Brief descriptions of the sampling and analytical procedures for each of these methodologies are provided in Appendix B. Table 6.2 summarizes the compounds for which method performance has been documented.

In order to minimize the number of methods required for a given monitoring program methods which apply to multiple compounds or even to multiple classes of compounds should be used. Table 6.1 indicates that four methods, TO-1, TO-2, TO-3, and TO-14, have the broadest application. With the exception of TO-4 and TO-10, which are designed for polychlorinated biphenyls and organochlorine pesticides, the remaining methods have limited application. Methods TO-1, TO-2, and TO-3 all employ solid sorbents, while Method TO-14 employs canisters. Methods TO-1 and TO-14 essentially represent the standard methods for TOAP monitoring programs and should be used whenever their application is appropriate.

Selection of an appropriate method will be affected by the monitoring plan considerations discussed in Section 3 of this document. In some cases, method performance will not be documented for compounds which are the focus of concern. This will require that the most appropriate method be selected and that method performance be validated for the compounds of interest. Alternatively, methods published by the National Institute of Occupational Safety and Health (NIOSH) or by the American Society of Testing and Materials (ASTM) can be used after appropriate validation for ambient studies.

TABLE 6.1

METHODS FOR THE ANALYSIS OF TOXIC ORGANIC AIR POLLUTANTS IN AMBIENT AIR

METHOD NUMBER	METHOD TITLE	POLLUTANT TYPES
TO-1	Determination of volatile organic compounds in ambient air, using Tenax^R adsorption and gas chromatography/mass spectroscopy	Volatile, nonpolar organics having boiling points in the 80° to 200°C range.
TO-2	Determination of volatile organic compounds in ambient air by carbon molecular sieve adsorption and gas chromatography/mass spectroscopy	Highly volatile, nonpolar organics having boiling points in the range of -15° to 120°C
TO-3	Determination of volatile organic compounds in ambient air, using cryogenic preconcentration techniques and gas chromatography with flame ionization and electron capture detection	Volatile, nonpolar organics having boiling points in the range of -10° to 200°C
TO-4	Determination of organochlorine pesticides and polychlorinated biphenyls in ambient air	Organochlorine pesticides and polychlorinated biphenyls
TO-5	Determination of aldehydes in ambient air, using high performance liquid chromatography	Aldehydes and ketones
TO-6	Determination of phosgene in ambient air, using high performance liquid chromatography	Phosgene
TO-7	Determination on N-nitrosodimethylamine in ambient air, using gas chromatography	N-nitrosodimethylamine
TO-8	Determination of phenol and methylphenols in ambient air, using high performance liquid chromatography	Cresol, Phenol

TABLE 6.1
(Continued)
METHODS FOR THE ANALYSIS OF TOXIC ORGANIC AIR POLLUTANTS IN AMBIENT AIR

METHOD NUMBER	METHOD TITLE	POLLUTANT TYPES
TO-9	Determination of polychlorinated dibenzo-p-dioxins (PCDD's) in ambient air, using high-resolution gas chromatography/high-resolution mass spectroscopy	Dioxins
TO-10	Determination of pesticides in ambient air, using low volume polyurethane foam sampling with gas chromatography/electron capture detection	Pesticides
TO-11	Determination of formaldehyde in ambient air, using DNPH-coated Sep-pak^R cartridge sampling with gas chromatography/electron capture detection	Formaldehyde
TO-12	Determination of non-methane organic compounds in ambient air, using cryogenic preconcentration and direct flame ionization detection	Non-methane organic compounds
TO-13	Methods of detection of benzo(a) pyrene and other polynuclear aromatic hydrocarbons in ambient air, using GC and HPLC	Polynuclear aromatic hydrocarbons
TO-14	Determination of volatile organic compounds in ambient air, using Summa^R-polished canisters and gas chromatographic analysis	Volatile organic compounds

TABLE 6.2

SAMPLING AND ANALYTICAL METHODOLOGIES FOR SELECTED TOXIC ORGANIC AIR POLLUTANTS

COMPOUND	APPLICABLE METHODS
Acetaldehyde	TO-5
Acrolein	TO-5
Acrylonitrile	TO-2, TO-3
Allyl Chloride	TO-2, TO-3
Aldrin	TO-4, TO-10
Benzaldehyde	TO-5
Benzene	TO-1, TO-2, TO-3, TO-14
Benzo(a)Pyrene	TO-13
Benzylchloride	TO-1, TO-3, TO-14
Bromoform (Tribromomethane)	TO-1, TO-3
Bromobenzene	TO-1
Bromomethane	TO-14
Captan	TO-10
Carbon Tetrachloride[2]	TO-1, TO-2, TO-3, TO-14
Chlordane	TO-10
Chlorobenzene	TO-1, TO-3, TO-14
Chloroethane	TO-14
Chloromethane	TO-14
Chloroform (Trichloromethane)[1]	TO-1, TO-2, TO-3, TO-14
Chlorothalonil	TO-10
Chlorpyrifos	TO-10
Cresols (o, m, p - Methyl Phenols)	TO-8
Cumene	TO-1
2,4,-D esters	TO-10
4,4'-DDE	TO-4, TO-10
4,4'-DDT	TO-4, TO-10
1,2-Dichlorobenzene	TO-14
1,3-Dichlorobenzene	TO-14
1,4-Dichlorobenzene	TO-1, TO-3, TO-14
Dichlorodifluoromethane	TO-14
1,2-Dichloroethane[1]	TO-1, TO-2, TO-3, TO-14
1,1-Dichloroethene	TO-2, TO-3, TO-14
cis-1,2-Dichloroethylene	TO-14
1,2-Dichloropropane	TO-1, TO-14
1,3-Dichloropropane	TO-1
cis-1,3-Dichloropropene	TO-14
trans-1,3-Dichloropropene	TO-14
1,2-Dichloro-1,1,2,2-tetrafluoroethane	TO-14
Dichlorvos (DDVP)	TO-10
Dicofol	TO-10
Dieldrin	TO-10
Endrin	TO-10

TABLE 6.2
(CONTINUED)
SAMPLING AND ANALYTICAL METHODOLOGIES FOR SELECTED TOXIC ORGANIC AIR POLLUTANTS

COMPOUND	APPLICABLE METHODS
Endrin Aldehyde	TO-10
Ethylbenzene	TO-1,TO-14
Ehylene Dibromide	TO-1, TO-14
4-Ethyltoluene	TO-14
Folpet	TO-10
Formaldehyde	TO-5, TO-11
Heptachlor	TO-10
Heptachlor epoxide	TO-10
1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin	TO-9
Hexachlorobenzene	TO-10
Hexachlorobutadiene	TO-14
and β-Hexachlorocyclohexanes	TO-10
Lindane	TO-10
Methoxychlor	TO-10
Methylene Chloride	TO-2, TO-3, TO-14
Mexacarbate	TO-10
Mirex	TO-10
Nitrobenzene	TO-1, TO-3
N-Nitrosodimethylamine	TO-7
trans-Nonachlor	TO-10
Octachlorodibenzo-p-Dioxin	TO-9
Oxychlordane	TO-10
Pentachlorobenzene	TO-10
Pentachlorophenol	TO-10
Phenol	TO-8
Phosgene	TO-6
Polychlorinated Biphenyls	TO-4
Propanal	TO-5
Ronnel	TO-10
Styrene	TO-14
1,2,3,4-Tetrachlorodibenzo-p-Dioxin	TO-9
2,3,7,8-Tetrachlorodibenzo-p-Dioxin	TO-9
1,1,2,2-Tetrachloroethane	TO-14
Tetrachloroethylene	TO-1, TO-3, TO-14
Toluene	TO-1, TO-2, TO-3, TO-14
1,2,4-Trichlorobenzene	TO-14
1,1,1-Trichloroethane[2]	TO-1, TO-2, TO-3, TO-14
1,1,2-Trichloroethane	TO-14
Trichlorofluoromethane	TO-14

TABLE 6.2
(CONTINUED)
SAMPLING AND ANALYTICAL METHODOLOGIES FOR SELECTED TOXIC ORGANIC AIR POLLUTANTS

COMPOUND	APPLICABLE METHODS
1,1,2-Trichloro-1,2,2-trifluoroethane	TO-14
2,4,5-Trichlorophenol	TO-10
1,2,4-Trimethylbenzene	TO-14
1,3,5-Trimethylbenzene	TO-14
Vinyl Chloride	TO-2, TO-3, TO-14
o, m, p-Xylene	TO-1, TO-3, TO-14

[1] TO-14 methodology has been validated with pressurized canisters only.

[2] Breakthrough volume using TO-1 is low.

SECTION 7

QUALITY ASSURANCE

7.1. QUALITY ASSURANCE EXPECTATIONS

As the discussion of Data Quality Objectives in Section 3 indicates, the environmental data used in a decision process must be (1) technically sound and defensible and (2) of sufficient quality to support the decision process. Achievement of DQO's is ultimately accomplished through a Quality Assurance (QA) program. An effective QA program for inclusion in a TOAP monitoring program will consist of planned and systematic activities necessary to establish consistency of the program output with the needs for which the program was established. Program needs can ultimately be understood in terms of acceptable uncertainty associated with the data; a QA program ensures that the limit of uncertainty is within the acceptable boundaries of the data collection program.

The limit of uncertainty will vary with the sampling and analytical procedures. Consequently, there is no universal QA performance standard applicable to all TOAP monitoring programs. It is therefore important to establish QA performance standards consistent with both the intended use of the data and the performance characteristics of the sampling and analysis procedures. Failure to reconcile discrepancies that exist between intended data use and QA performance characteristics of the sampling and analytical protocol will undermine the TOAP monitoring program.

7.2 QUALITY ASSURANCE AND QUALITY CONTROL

QA is essentially a management program that addresses delegation of program responsibilities to individuals, documentation, data review, and audits. The objective of QA procedures is to permit an assessment of the reliability of the data. QA activities are typically performed by personnel involved in normal routine operations.

Quality Control (QC) activities complement QA activities. QC activities address sampling procedures, sample integrity, analysis methods, calibration procedures, equipment maintenance procedures, and data production. QC procedures are also performed by individuals involved in the normal routine operations.

7.3 QUALITY ASSURANCE MANAGEMENT

A QA program is essentially a management tool used to ensure that data collected is continually consistent with predetermined quality limits. The major elements of an effective QA program included in a TOAP monitoring program are discussed in the following subsections.

7.3.1 Quality Assurance System Design

Three fundamental elements comprise an effective QA program: First, QA policy and quantitative quality goals or objectives must be defined in a written QA plan. Secondly, organizational structure must accommodate a QA function through job assignments and communication mechanisms. Third, individuals associated with the QA function must have written job descriptions, duties, responsibilities, and authority commensurate with their intended function. Each of these vital QA program components is discussed below:

Before a QA program can be developed, it is necessary to establish a QA policy and establish the objectives of the QA program. Once these fundamental tasks have been accomplished, a QA program can be written to address the strategy for achieving definitive quality objectives relevant to the activities of the organization.

Strategic QA program planning will obviously require an organizational structure conducive to effective QA management. Appropriate considerations for organizational structure include personnel assignments and communication.

Effective QA is accomplished by a separate individual or group within the organization. The individual(s) responsible for QA will have written job descriptions and the corresponding duties, responsibilities, and authority to perform their job functions in a manner that satisfies the QA program requirements.

Although individuals associated with the QA functions are removed from the routine operations they are responsible for assessing, they are by no means totally isolated from those routine operations. Open lines of communication and established communication practices are necessary to ensure interaction between QA personnel, personnel generating data, and personnel assimilating the data. Effective communication is therefore essential to the QA program and will ensure that QA functions are adequately reflected in data output.

7.3.2 Document Control

Because of the volume of written information associated with a TOAP monitoring program, it is necessary to establish procedures for document control, consisting of written procedures for inspection, review, revision, and archival of monitoring program documents. Document control procedures are generally applicable to the following:

- Sampling procedure.
- Calibration procedure.
- Analytical procedure.
- Data analyses, validation, and reporting procedure.
- Performance and system audit procedure.

- Preventive maintenance procedure.
- The QA program plan.
- QA plans for specific projects
- Laboratory record notebooks.
- Data sheets.

7.3.3 Data Evaluation

The intent of a QA program is to maintain data continuously within pre-determined quality limits. This objective will not be achieved if information applicable to a QA management activity is not received, reviewed, and/or acted on in a timely manner. An effective QA program will therefore establish what information is required by QA management personnel, how it will be used, when it will be required, when it will be reviewed, and when control actions necessitated by unacceptable data will be implemented.

7.3.4 Standard Reference Materials

The fundamental requirements for producing reliable data are appropriate methodology and properly calibrated instrumentation used according to established procedure. The quality of generated data can be assessed by incorporating reference materials into the sampling and analytical processes.

A reference material is a substance for which critical properties are sufficiently well established for the reference material to be used to calibrate an analyzer or validate a measurement process. Generally speaking, there are three types of reference materials in common use: An internal reference material (ICM) is developed by a laboratory for its own internal use. A certified reference material (CRM) is a reference material issued by an organization recognized by practicing professionals as technically competent to do so. A Standard Reference Material (SRM) is a certified reference material issued by the National Institute of Standards and Technology (NIST). All three types of reference materials are integral components of effective QA programs for TOAP monitoring projects. SRM's are particularly important because they are traceable to national standards and, if used as primary standards, allow meaningful comparisons of data generated by different laboratories or by different sampling and analytical procedures.

SRM's for toxic organic air pollutants at sub PPM and PPB levels were unavailable until recently. Within the past two years SRM's for several TOAP's at the 5 ppb level have been developed as multi-component mixtures. Information concerning these materials is provided in Appendix E. Whenever possible, these SRM's should be incorporated into the QA program for a TOAP monitoring project.

7.3.5 Quality Audits

Quality auditing tasks are similar to quality control tasks and in some instances may be identical. The significant difference between quality auditing and quality control tasks is that the former are administered by individuals who are not directly involved with the measurement process.

7.3.5.1 Performance Audits

Performance audits are incorporated into a TOAP monitoring program to quantitatively assess the quality of the data being generated by a measurement system. Performance audits include the evaluation of recovery of reference materials through the sampling and analytical equipment and the review of results when test data are entered into a data processing system.

7.3.5.2 System Audits

System audits are incorporated into a TOAP monitoring program to qualitatively assess the quality of data being generated by the measurement system. System audits focus on operational aspects of the measurement process. There aspects include adherence to (a) established sampling and analytical procedures, (b) sample shipment and receipt procedures, (c) equipment maintenance schedules, and (d) quality control and quality audit schedules.

7.3.6 Quality Assurance Reports

A variety of QA reports should be prepared periodically by the QA personnel and submitted to the TOAP monitoring program manager. The frequency and type of report required will be specified by the QA project plan.

Data Quality Assessment Reports address the precision and accuracy of program data. Performance and System Audit Reports summarize the results of audits performed during the course of the TOAP monitoring project. Data Validation Reports summarize questionable data collected during the monitoring program, the results of follow-up investigations concerning such data, data corrected or rejected as a result of the investigation, corrective action recommended, and effectiveness of the data validation procedures. Quality Cost Reports summarize the costs associated with each element (prevention, appraisal, and failure) of a Quality Cost System for a TOAP monitoring program. Instrument and/or Equipment Downtime Reports summarize information concerning instrument and/or equipment failures, failure courses, repair time, and total downtime. Control Charts are graphical representations of QA Data. Finally, Interlaboratory Comparison Summary Reports are published by EPA and are applicable only to specific analytes and methodologies.

7.3.7 Corrective Action

In many cases data review or audit procedures will result in the need for corrective action. This may involve reporting certain aspects of the work or simply providing more detailed documentation for work already performed. In either case QA management will be responsible for documenting the need for, type of, and implementation of corrective action.

7.3.8 Training

An important component of a QA program will involve personnel training. Trained personnel are necessary to ensure that the data they produce are complete and of high quality. Training can be accomplished on the job or by trainees attending courses relevant to the employees' job functions.

The effectiveness of training must be documented to establish and maintain the integrity of the training program. Training effectiveness can be evaluated by written tests, proficiency evaluations, and/or interviews.

7.4 SAMPLING QUALITY ASSURANCE

The purpose of sampling is to collect unbiased samples that are representative of the system being monitored. The sampling program should be planned and documented in all details. QA for sampling includes site selection, number of samples to be collected, frequency of sample collection, sampling times, instrument calibration and maintenance, Quality Control sample collection, data recording, sample labeling, sample preservation, sample storage, sample transport, and chain-of-custody procedures.

7.4.1 Site Selection

Site selection planning is discussed thoroughly in Section 3.3. The QA plan for a TOAP monitoring program should specify factors which could result in modification of the siting plan during the monitoring effort, procedures for approving such modifications, and provisions for documenting sampling site modifications.

7.4.2 Instrument Calibration and Maintenance

Calibration of sampling equipment is as vital as calibration of analytical equipment if meaningful data concerning ambient concentrations of TOAP's are to be obtained. A QA plan for a TOAP monitoring program will therefore address calibration of sampling equipment. Typically the QA plan will include:

- Written calibration procedures.
- Calibration frequencies.
- Acceptable calibration quality.
- A statement of the appropriate environment in or conditions for which the sampling equipment can be used.
- Provisions for proper record keeping of calibration data.

The QA plan will also address appropriate maintenance activities and frequencies for sampling equipment, to ensure that it operates as planned. Additionally, the QA plan will address procedures to document performance of maintenance activities on schedule.

7.4.3 Routine Quality Control Sample Collection

A QA plan for a TOAP monitoring project will include a provision for the collection of a variety of quality control samples. Quality control samples to check overall system performance may include replicate or split samples, spiked samples, standard reference materials, blanks, and backup snipes (e.g. series impingers or resin cartridges). Split or replicate samples are useful checks on sampling and analysis precision and should be included with each group of samples. Field blanks, in which the sampling activity is duplicated exactly except that no air is sampled, should also be routinely collected. Backup samples should be collected whenever the recovery performance of a particular sampling medium has not been documented or is subject to wide variations depending on ambient conditions. Spiked samples should be included whenever an accurate spiking procedure is available, provided that the spiked material reasonably simulates the physical and chemical state of the native material.

7.4.4 Sample Labeling, Preservation, Storage, and Transport

The data obtained from a TOAP monitoring program will be meaningless if samples are improperly labeled or if preservation, storage, or transport procedures are inappropriate for the required analyses. Sample labeling, preservation, storage, and transport procedures will therefore be specified in the QA plan, and these procedures should be carefully explained to field personnel, prior to sampling, to ensure proper implementation. Sample labels, prepared in advance, should include sufficient information to associate a given sample with a particular data sheet, as well as with the overall program record notebook. In general, each sample should be given a unique identification number with a prefix describing the type of sample.

7.4.5 Chain-of-Custody Procedure

Chain-of-custody procedures are used to document the movement of a sample from collection until analysis, to ensure sample integrity. Formal chain-of-custody requirements place a substantial burden on both field and laboratory personnel. Chain-of-custody procedures must be documented in the QA plan for a TOAP monitoring project and reviewed with the personnel who will use them, to ensure that the data is fundamentally legally defensible.

7.5 ANALYTICAL QUALITY ASSURANCE

The QA plan for the analytical component of a TOAP monitoring program will address method validation requirements, instrument maintenance and calibration, quality control sample analysis, and data recording. Each of these aspects is discussed in the subsections that follow.

7.5.1 Method Validation

Many TOAP monitoring programs will require the development of new or modification of existing sampling and analytical protocols. It will be necessary to establish the performance characteristics of these procedures, prior to their use in TOAP monitoring programs. Performance characteristics will include determination of precision, accuracy, detection limit, and specificity through the analysis of laboratory standards and, whenever possible, representative samples. The validation requirements should be appropriate. The incorporation of SRM's in the method validation process will prove cost effective and minimize the time required to bring a new method on line. It is important to validate the method in a manner that approximates as closely as possible the conditions that will exist when actual samples are collected.

Performance criteria for existing, well documented methodologies must also be validated when a procedure is used for the first time by the test team. Validation of this type will require the development of a data base sufficient to establish critical statistical parameters such as the coefficient of variation. Again, SRM's are a key component of the method validation process.

Finally, method validation procedures, such as the recovery of spiked samples, should be integrated into the daily sampling and analysis program. SRM's, IRM's, or CRS's are appropriate for this form of method validation.

7.5.2 Instrument Calibration and Maintenance

Proper calibration of analytical instrumentation is fundamental to the success of a TOAP monitoring program. The QA plan for a TOAP monitoring program will therefore include a calibration plan for the various analytical systems used on the project. The calibration plan will include:

1. A statement of the maximum allowable time between multipoint calibrations and calibration checks.

2. A statement of the minimum quality of calibration standards (e.g. standards should have four to ten times the accuracy of the instruments that they are being used to calibrate). A list of calibration standards should be provided.

3. Provisions for standard traceability (e.g., standards should be traced to NBS-SRM's or commercial Certified Reference Materials [CRM's] if available).

4. Provisions for written procedures to help ensure that calibrations are always performed in the same manner. The procedures should include the intended range of validity.

5. Statement of proper environmental conditions, to ensure that the equipment is not significantly affected by its surroundings.

6. Provisions for proper record keeping and record forms to ensure that adequate documentation of calibrations is available for use in internal data validation and in case the data are used in enforcement actions.

7. Documentation of qualifications and training of personnel performing calibrations.

The QA plan will also address appropriate maintenance activities and frequencies for analytical equipment. Additionally, the QA plan will include procedures to document performance of maintenance activities on schedule.

7.5.3 Quality Control Sample Analysis

A QA plan for a TOAP monitoring project will include provisions for the analysis of a variety of quality control samples. Quality control samples for evaluating analytical performance should include blanks, spiked process blanks, spiked samples, standard reference materials, and replicate (or split) samples. Standard reference materials and replicate or split samples should generally be included as part of field QA and need not be additionally included at the analysis stage. However, additional blanks, spiked process blanks, and spiked samples should be included, since this practice allows matrix effects to be distinguished from analytical losses.

7.6 DATA MANAGEMENT

The QA plan for a TOAP monitoring program will include procedures designed to ensure that required sampling and analytical data are captured and maintained securely and efficiently. Data recording procedures that should be specified in the sampling QA plan include (a) periodic reading of the temperature, flow, volumes, and other parameters; (b) documentation of meteorological conditions at appropriate time points; (c) documentation of instrument operating variables; (d) documentation of any upset conditions such as sudden leakage or pressure surges; and (e) documentation of calibration or maintenance activities. A logbook for the overall sampling program, in which sampling descriptions, meteorological data, and upset conditions are documented, should be maintained. A data sheet should also be prepared for each set of samples or analytical procedure for which relevant raw data should be recorded. Certain measurements, such as filter numbers and weights or impinger volumes, which are required for analytical purposes can be recorded on a separate sheet with provisions for recording subsequent analytical data on the same sheet. Separate maintenance and calibration logbooks should be maintained for each instrument. In most cases, specific sampling data forms for a given program must be prepared because of differences in the sampling design between programs.

The QA program for a TOAP monitoring project will address various steps in the data reduction process including:

- Merging sampling and analytical data.

- Storage of raw and intermediate data.

- Data validation.

Since sampling and analytical data processing occurs independently in most cases, the QA plan will address the manner in which data from the two activities are to be treated and validated during the reduction process. Because TOAP monitoring data can be collected over an extended period of time and may involve several parties, it is important that the QA plan address procedures for transferring and storing raw and intermediate data. Finally, the data reduction component of the QA program will set up data validation procedures so that appropriate data validation reports can be prepared.

7.7 REPORTING QUALITY ASSURANCE

The report represents the final output of a TOAP monitoring program. The QA plan will therefore incorporate appropriate review procedures to ensure that the report properly summarizes the results of the study.

The report must be reviewed by individuals capable of recognizing technical deficiencies and QA inconsistencies. The report should also be reviewed by project personnel who were involved in data generation. Finally, the report should be reviewed for editorial content, to minimize ambiguities.

REFERENCES

1. List of Air Pollutants Subject to the Provisions of Section 112 of the Clean Air Act. U.S. Government: Printing Office, Washington, D.C., 1987.

2. Singh, H. B., L. J. Salas, A. Smith, R. Stiles, and H. Shingeishi. Atmospheric Measurements of Selected Hazardous Organic Chemicals. EPA-600/53-81-031 (PB81-200-628). U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1981.

3. Air Pollution, A. C. Stern, ed., 2nd Edition, V. II, Academic Press, New York, 1968. pp. 329-391.

4. NIOSH Manual of Analytical Methods, Parts 1-3. 2nd Edition, National Institute for Occupational Safety and Health, Cincinnati, Ohio, 1977.

5. Annual Book of Standards. Part 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials, Philadelphia, Pennsylvania. (Published Annually)

6. Methods of Air Sampling and Analysis, M. Katz, ed., 2nd Edition, American Public Health Association, Washington, D.C., 1977.

7. Riggin, R. M. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. EPA-600/4-84-041. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1984.

8. Air Pollution, A. C. Stern, ed., 3rd Edition, V. III, Academic Press, New York, 1976. pp. 344-368.

9. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). EPA-450/4-80-012 (PB 81-153231). U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1980. 45 pp.

10. Quality Assurance for Air Pollution Measurement Systems, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1976. V. I - Principles, EPA-600/9-76-005. V. II Ambient Air Specific Methods, EPA-600/4-77-027a.

11. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, QAMS-005/80, U.S. Environmental Protection Agency, Washington, D.C., December 29, 1980.

12. Handbook of Chemistry and Physics, Chemical Rubber Company, Cleveland, Ohio. (Published Annually)

13. Lange's Handbook of Chemistry, McGraw-Hill Book Company.

14. The Merck Index, Merck and Co., Rahway, New Jersey. (Published Annually)

15. Handbook of Environmental Data on Organic Chemicals, K. Verschueren, ed., Van Nostrand and Co., New York, 1977. 659 pp.

16. Spicer, C. W., M. W. Holdren, L. E. Slivon, R. W. Coutant, and D. S. Shadwick. Intercomparison of Sampling Techniques for Toxic Organic Compounds in Indoor Air. EPA/RTP, NC. EPA-600/4-87-008. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1987.

17. Comparison of Tenax and Canister Sampling Techniques for Volatile Organic Compounds in Ambient Air. Battelle Columbus Division. 1987.

18. Chuang, J. C., S. W. Hannan, and N. K. Wilson. Field Comparison Study of Polyurethane Foam and XAD-2 Resin for Air Sampling of Poly Aromatic Hydrocarbons. EPA, APCA Symposium on Measurement of Toxic and Related Air Pollution. 1987.

19. DeRoos, F. L., J. E. Tabor, S. E. Miller, S. C. Watson, and J. A. Hatchel. Evaluation of an EPA High-Volume Sampler for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. EPA-600/4-86/037. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1987.

20. Lane, D. A. and D. M. A. McCurvin. A Personal Computer Database for the Chemical, Physical and Thermodynamic Properties of the Polycyclic Aromatic Compounds. EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, 1987. pp 341-43.

21. Clements, J. B. and R. G. Lewis. Sampling for Organic Compounds. EPA/600/p-87/052. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1987. p. 11.

22. Standard Practice for Application of the Hi-Vol Sampler method for Collection and Mass Determination of Airborne Particulate Matter. Annual Book of ASTM Standards. Amer. Soc. Test. Mater., Designation D 4096-82, Phil., PA.

23. Phillips, J. B., J. R. Valentin and G. C. Carle. Large Volume Sampling Without Preconcentration for Continuous Gas Chromatography. Toxic Materials in the Atmosphere, ASTM STP, 786, 1982. pp. 135-141.

24. Reference 6, pp. 38-48.

25. Handy, R. W., H. L. Crist, and T. W. Stanley. Quality Assurance for Personal Exposure Monitoring. ASTM Special Technical Publication No. 867, 1985.

26. Walling, J. F., J. E. Bumgarner, D. J. Driscoll, C. M. Morris, A. E. Riley, and L. H. Wright. Apparent Reaction Products Desorbed from Tenax Use to Sample Ambient Air. Atmos. Enviro., 20 (1). 1986. pp. 51-57.

27. DRAFT EMSL/RTP Protocol. Sampling Air for Volatile Organic Compounds Using Tenax.

28. Chuang, J. C., W. E. Bresler, and S. W. Hannan. Evaluation of Polyurethane Foam Cartridges for Measurement of Polynuclear Aromatic Hydrocarbons in Air. EPA-600/54-85/055. U.S. Environmental Protection Agency, Research Triangle Park, 1985.

29. Coppi, S., A. Betti and M. Ascanelli. Styrene Copolymers as Pollutant Adsorbents Safe Sampling Volume. J. Chromatog., 390, 1987. pp. 349-355.

30. Williams, E. J., and R. E. Sievers. Synthesis and Characterization of a New Sorbent for Use in the Determination of Volatile, Complex - Farming Organic Compounds in Air. Anal. Chem. 56-1984. pp. 2523-2528.

31. Kebbekus, B. B., and J. W. Bozzelli. Collection and Analysis of Selected Volatile Organic Compounds in Ambient Air. Proc. Air Pollution Control Assoc., Paper No. 82-65.2. Air Poll. Control Association, Pittsburgh, Pennsylvania, 1982.

32. Holzer, G., H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield, and H. M. Liebich. Collection and Analysis of Trace Organic Emissions from Natural Sources. J. Chromatog. 142, 1977. pp. 755-764.

33. Reference 3 pp 156-158.

34. Cobb, G. P., R. S. Braman, and K. M. Hua. Carbon Hollow Tubes as Collectors in Thermal Resorption/Gas Chromatographic Analysis of Atmospheric Organic Compounds. Anal. Chem., 58, 1986. pp. 2213-221.

35. Hawthorne, S. B., and D. J. Miller. Extraction and Recovery of Organic Pollutants from Environmental Solids and Tenax-GC Using Supercritical CO_2. J. Chromato. Sci., 24, 1986. pp. 258-263.

36. Krasnec, J. P. Grab Sampling as an Effective Tool in Air Pollution Monitoring. EPA, APCA Symposium on Measurement of Toxic and Related Air Pollutants, RTP, NC., 1987.

37. Oliver, K. D., J. D. Pleil, and W. A. McClenny. Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in Summa^R Polished Canisters. Atmos. Environ., 20 (7), 1986. pp. 1403-1441.

38. Holden, M. W., D. L. Smith, and W. A. McClenny. A Prototype Sampler for Preconcentration and Transferring Volatile Organic Compounds from Ambient Air to Passivated Canisters. EPA, APCA Symposium on Measurement of Toxic and Related Air Pollutants, RTP, NC., 1987.

39. Holdren, M., S. Humrickhouse, S. Truitt, H. Westberg, and H. Hill. Analytical Technique to Establish the Identity and Concentration of Vapor Phase Organic Compounds. Proc. Air Poll. Control Assoc., Paper No. 79-52.2, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1979.

40. McElroy, F. F., V. C. Thompson, and H. G. Richter. A Cryogenic Preconcentration - Direct FID (PDFID) Method for Measurement of NMOC in Ambient Air. EPA-600/4-85/063. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1985.

41. Reference 3, pp 152-154.

42. Fung, K., and D. Grosjean Determination of Nanogram Amounts of Carbonyls as 2,4-Dinitrophenylhydrazones by HPLC. Anal. Chem. 53, 1981. pp. 168-171.

43. Kring, E. V. et. al. Pro-Tek Organic Vapor Air Monitoring Badges. Toxic Materials in the Atmosphere, ASTM STP 786, 1982. pp. 85-103.

44. Brown, R. H., P. C. Cox, C. J. Purnell, N. G. West, and M. D. Wright. The Application of Passive Sampling Techniques to the Analysis of Specific Vapors in Air. In: Identification and Analysis of Organic Pollutants in Air, L. H. Keith, ed., Ann Arbor Science, 1984. pp. 37-49

45. Levin, J. O, R. Lindahl, and K. Anderson. A Passive Sampler for Formaldehyde in Air Using 2.4 - Dinitrophenylhydrazin-Coated Glass Fiber Filters. Environ. Sci. Technol., 20, 1986. pp. 1273-1276.

46. Thompson, J. M. and W. I. Stephen. Comparison of Recoveries of Trichloroethylene from Charcoal Tubes and Thermally-Desorbably Personal Monitors. Anal. Chem. Acta., 182, 1986. pp. 299-302.

47. Tuan, Vo-Dinh. Development of a Dosimeter for Personnel Exposure to Vapors of Polyaromatic Pollutants. Enviro. Sci. Tech., 19, 1985. pp. 997-1003.

48. Reference 3, pp 3-47.

49. Reference 6, pp 191-205.

50. Kolak, N. P., and J. R. Visalli. Comparison of Three Methods for Measuring Suspended Particulate Concentrations. Env. Sci. Tech, 15, 1981. pp. 219-224.

51. Mitchell, R. I., W. M. Henry, and N. C. Henderson. "Mega-volume Respirable Particulate Sampler (Mark II)". Proc. Air Poll. Control Assoc., Paper No. 77-35.1, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1977.

52. Colson, E. R. "Flame Ionization Detectors and High-End Linearity." Anal. Chem., 58, 1986. pp. 337-344.

53. Lewis, R. G. Development of New Sampling and Analysis Techniques For Hazardous Air Pollutants in Ambient and Indoor Air. Internal Report FY-87 EMSL/RTP, NC., Dec. 1987.

54. Foreman, W. T. and T. F. Bidleman. An Experimental System for Investigating Vapor-Particle Partitioning of Trace Organic Pollutants. Environ. Sci. Technol., 21, 1987. pp. 869-875.

55. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, 2nd Edition, EPA 600/4-78-201. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1978.

56. Reference 6, pp 184-186.

57. Ibid. pp 88-98.

58. Gas Chromatography with Glass Capillary Columns, Jennings, W., ed., Academic Press, New York, 1978.

59. Recent Advances in Capillary Gas Chromatography, Bertsch, W., G. Jennings, and R. E. Kaiser, ed., Verlag, Heidelberg, 1981.

60. Cox, R. D., and R. F. Earp. Determination of Trace Level Organics in Ambient Air by High Resolution Gas Chromatography with Simultaneous Protoionization and Flame Ionization Detection. Anal. Chem., 54, 1982. pp. 2265-2270.

61. Pellizari, E. D. Electron Capture Detection in Gas Chromatography. J. Chrom., 98, 1974. pp. 323-361.

62. Freedman, A. N. Photoionization Detector Response. J. Chrom., 236, 1982. pp. 11-15.

63. McFaden, W. H. Techniques of Combined Gas Chromatography Mass Spectrometry, John Wiley and Sons, New York, 1973.

64. Lane, D. A. Mobile Mass Spectrometry. Env. Sci. Tech. 16, 1982. pp. 38A-46A.

65. Burlingame, A. L., A. Dell, and D. H. Russel. Gas Chromatography Mass Spectrometry. Anal. Chem. 54, 1982. pp. 363R-409R.

66. Krost, K., E. D. Pellizzari, S. G. Walbun, and S. A. Hubbard. Collection and Analysis of Hazardous Organic Emissions. Anal. Chem. 54, 1982. pp. 810-818.

67. Introduction to Modern Liquid Chromatography, Snyder, L. R., and J. J. Kirkland, 2nd Edition, John Wiley and Sons, New York, 1979.

68. Reference 6, pp. 248-256.

69. Ibid. pp 128-136.

70. Ibid. pp 216-219.

71. Shafer, K. H., M. Cooke, F. DeRoos, R. J. Jakobsen, O. Rosario, and J. D. Mulik. WCOT Capillary Column GC/FT-IR and GC/MS for Identifying Toxic Organic Pollutants. Applied Spectroscopy, 35, 1981. pp. 469-472.

72. Tuazon, E. C., A. M. Winer, R. A. Graham, and J. N. Pitts. Atmospheric Measurements of Trace Pollutants by Kilometer-Pathlengths FT-IR Spectroscopy. In Advances in Environmental Science and Technology, 10, 1980. pp. 259-300.

APPENDIX A

COMPOUNDS SUBJECT TO REGULATION UNDER THE PROPOSED CLEAN AIR ATTAINMENT ACT OF 1987

TABLE 1.A

CAS Number	Substance
75-07-0	Acetaldehyde
60-35-5	Acetamide
67-64-1	Acetone
75-05-8	Acetonitrile
53-96-3	2-Acetylaminofluorene (N-9H-fluoren-2-YL-acetamide)
107-02-8	Acrolein
79-06-1	Acrylamide
79-10-7	Acrylic acid
107-13-1	Acrylonitrile
309-00-2	Aldrin
107-05-1	Allyl chloride
7429-90-5	Aluminum (fume or dust)
96-67-1	4-Aminobiphenyl
7664-41-7	Ammonia
62-53-3	Aniline
90-04-0	o-Anisidine
104-94-9	P-Anisidine
7440-36-0	Antimony (and compounds)
7440-38-2	Arsenic (and compounds)
1332-21-4	Asbestos (friable)
492-80-8	Auramine
7440-39-3	Barium (and compounds)
71-43-2	Benzene
92-87-5	Benzidine
50-32-8	Benzo[a]pyrene
98-07-7	Benzoic trichloride (Bensotrichloride)
94-36-0	Benzoyl peroxide
100-44-7	Benzyl chloride
7440-41-7	Beryllium (and compounds)
92-52-4	Biphenyl (Diphenyl)
111-44-4	Bis (2-chloroethyl) ether (2,2'-Dichloroethyl ether)
75-25-2	Bromoform (Tribromomethane)
74-83-9	Bromomethane (Methyl bromide)
106-99-0	1,3-Butadiene
141-32-2	Butyl acrylate
71-36-3	n-Butyl alcohol (1-Butanol)
78-92-2	sec-Butyl alcohol
85-68-7	Butyl benzyl phthalate
123-72-8	Butyraldehyde

TABLE A.1
(CONTINUED)

CAS Number	Substance
7440-43-9	Cadmium (and compounds)
156-62-7	Calcium cyanamide
133-06-2	Captan
63-25-2	Carbaryl
75-15-0	Carbon disulfide
56-23-5	Carbon tetrachloride
120-80-9	Catechol (Pyrocatechol)
133-90-4	Chloramben
57-74-9	Chlordane
76-13-1	Chlorinated fluorocarbon (Freon 113)
7782-50-5	Chlorine
10049-04-4	Chlorine dioxide
79-11-8	Chloroacetic acid (Assistacetic acid)
532-27-4	2-Chloroaceto phenone (a-Chloroacetophenone)
108-90-7	Chlorobenzene
510-15-6	Chlorobenzilate (Ethyl 4-4′-dichlorobenzilate)
75-00-3	Chloroethane (Ethyl Chloride)
67-66-3	Chloroform
74-87-3	Chloromethane (Methyl chloride)
542-88-1	Chloromethyl ether
107-30-2	Chloromethyl methyl ether
126-99-8	Chloroprene
7440-47-3	Chromium (and compounds)
7440-48-4	Cobalt (and compounds)
7440-50-8	Copper (and compounds)
1319-77-3	Cresol (mixed isomers)
108-39-4	m-Cresol
95-48-7	o-Cresol (o-Cresyl acid)
106-44-5	p-Cresol
98-82-8	Cumene (1-Methylbenzene)
57-12-5	Cynanide compounds
110-82-7	Cyclohexane (Hexahydrobenzene)
94-75-7	2,4-D ((2,4-Dichlorophenoxy) Acetic acid)
72-55-9	DDE
25376-45-8	Diaminotoluene (mixed isomers)
95-80-7	2,4-Diaminotoluene
119-90-4	0-Dianisidine (3.3′-Dimethoxybenzidene)
334-88-3	Diazomethane
132-64-9	Dibenzofuran

TABLE A.1
(CONTINUED)

CAS Number	Substance
96-12-8	1,2-Dibromo-3-chloropropane (DBCP)
106-93-4	1,2-Dibromoethane (Ethylene dibromide)
84-74-2	Dibutyl phthalate
25321-22-6	Dichlorobenzene (mixed isomers)
95-50-1	1,2-Dichlorobenzene (o-Dichlorobenzene)
106-46-7	1,4-Dichlorobenzene (p-Dichlorobenzene)
91-94-1	3,3'-Dichlorobenzidine
75-71-8	Dichlorofluoromethane
75-34-3	1,1-Dichloroethane
107-06-2	1,2-Dichloroethane (Ethylene Dichloride)
540-59-0	1,2-Dichloroethylene (Acetylene dichloride)
75-09-2	Dichloromethane (Methylene Chloride)
78-87-5	1,2-Dichloropropane
542-75-6	1,3-Dichloropropylene (1,3-Dichloropropene)
62-73-7	Dichlorvos
115-32-2	Dicofol (Kelthane)
60-57-1	Dieldrin
111-42-2	Diethanolamine
117-81-7	Di(2-Ethylhexyl) phthalate (DEHP)
84-66-2	Diethyl phthlate (1,2-Diethyl ester 1,2-benzene dicarboxy)
64-67-5	Diethyl sulfate
60-11-7	4-Dimethylaminoazobenzene (p-Dimethylaminoazobenzene)
121-69-7	N, N-Dimethylaniline
119-93-7	3.3'-dimethylbenzidine (o-Tolidine)
79-44-7	Dimethylcarbamyl chloride
57-14-7	1,1-Dimethyl hydrazine (Dimethyldydrazine)
131-11-3	Dimethyl phthalate
77-78-1	Dimethyl sulfate
534-52-1	4,6-Dinitro-o-cresol (Dinitrocresol)
51-28-5	2,4-Dinitrophenol

TABLE A.1
(CONTINUED)

CAS Number	Substance
121-14-2	2,4-Dinitrotoluene (1-Methyl-2, 4-Dinitrobenzene)
123-91-1	1,4-Dioxane (1,4-Diethylene dioxide)
122-66-7	1,2-Diphenyl hydrazine (Hydrazobenzene)
106-89-8	Epichlorohydrin
110-80-5	2-Ethoxyethanol
140-88-5	Ethyl acrylate
100-41-4	Ethyl benzene
74-85-1	Ethylene
107-21-1	Ethylene glycol
151-56-4	Ethyleneimine (Azindine)
75-21-8	Ethylene oxide
96-45-7	Ethylene thiourea
50-00-0	Formaldehyde
76-44-8	Heptachlor
118-74-1	Hexachlorobenzene
87-68-3	Hexachloro-1,3-butadiene
77-47-4	Hexachlorocyclopentadiene
67-72-1	Hexachloroethane
1335-87-1	Hexachloronaphthalene
680-31-9	Hexamethylphosphoramide
302-01-2	Hydrazine
7647-01-1	Hydrochloric acid (Hydrogen chloride [gas only])
74-90-8	Hydrogen cyanide (Hydrocyanic acid)
7664-39-3	Hydrogen fluoride
123-31-9	Hydroquinone
78-59-1	Isophorone
67-63-0	Isopropyl alcohol (Mfg.-strong acid processes)
7439-92-1	Lead (and compounds)
58-89-9	Lindane (Hexachlorocyclohexane)
108-31-6	Maleic acid anhydride (2,5-Furandione)
7439-96-5	Manganese (and compounds)
51-75-2	Mechlorethamine (Nitorgen mustard)
108-78-1	Melamine
7439-97-6	Mercury (and compounds)
67-56-1	Methanol
72-43-5	Methoxychlor (1,1,1-Trichloro-2,2-Bis [P-Methoxyphenyl] ethyl)

TABLE A.1
(CONTINUED)

CAS Number	Substance
109-86-4	2-Methoxyethanol (Methyl cellosolve)
96-33-3	Methyl acrylate
101-14-4	4,4'-Methylene bis (2-Chloroaniline) (MOCA)
101-68-8	Methylene bis(Phenylisocyanate) (MBI)
101-77-9	4,4'-Methylene dianiline (p,p'-diaminodiphenylmethane)
78-93-3	Methyl ethyl ketone (MEK) 2-Butanone)
60-34-4	Methyl hydrazine
74-88-4	Methyl iodide (Iodomethane)
108-10-1	Methyl isobutyl ketone (MIBK) (Isopropylacetone) (Hexone)
624-83-9	Methyl isocyanate
80-62-6	Methyl methacrylate
91-20-3	Naphthalene
134-32-7	alpha-Naphthylamine
91-59-8	beta-Naphthylamine (2-Naphthylamine)
7440-02-0	Nickel (and compounds)
7697-37-2	Nitric acid
98-95-3	Nitrobenzene
92-93-3	4-Nitrobiphenyl
1836-75-5	Nitrofen
55-63-0	Nitroglycerin
100-02-7	4-Nitrophenol
79-46-9	2-Nitropropane
62-75-9	N-Nitrosodimethylamine
684-93-5	N-Nitroso-N-methylurea (N-methyl-N-nitrosocarbamide)
59-89-2	N-Nitrosomorpholine
2234-13-1	Octachloronaphthalene
20816-12-0	Osmium tetroxide
56-38-2	Parathion
87-86-5	Pentachlorophenol (PCP)
108-95-2	Phenol
106-50-3	p-Phenylenediamine
75-44-5	Phosgene
7664-38-2	Phosphoric acid
7723-14-0	Phosphorus (yellow or white)
85-44-9	Phthalic anhydride (1,2 Benzene dicarboxylac acid anhydride)
88-89-1	Picric acid

TABLE A.1
(CONTINUED)

CAS Number	Substance
1336-36-3	Polychlorinated biphenyls (PCB's)
1120-71-4	Propane sultone (2,2-dioxide 1,2-oxathiolane)
57-57-8	beta-Propiolactone
114-26-1	Propoxur
75-55-8	Propyleneimine
75-56-9	Propylene oxide
110-86-1	Pyridine
91-22-5	Quinoline
106-51-4	Quinone (p-Benzoquinone)
82-68-8	Quinotozene (Pentachloronitrobenzene)
7782-49-2	Selenium
7440-22-4	Silver (and compounds)
1310-73-2	Sodium hydroxide (solution)
100-42-5	Styrene (monomer)
96-09-3	Styrene oxide
7664-93-9	Sulfuric acid
100-21-0	Terephthalic acid
1746-01-6	2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD)
79-34-5	1,1,2,2-Tetrachlorethane
127-18-4	Tetrachloroethylene (Perchloroethylene)
7440-28-0	Thallium (and compounds)
13463-67-7	Titanium dioxide
108-88-3	Toluene (Methyl benzene)
584-84-9	Toluene-2,4-Diisocyanate
95-53-4	o-Toluidine
8001-35-2	Toxaphene (Camphechlor)
120-82-1	1,2,4-Trichlorobenzene
71-55-6	1,1,1-Trichlorethane (Methyl chloroform)
79-00-5	1,1,2-Trichloroethane
79-01-6	Trichloroethylene (Trichloroethene)
95-95-4	2,4,5-Trichlorophenol
88-06-2	2,4,6-Trichlorophenol
1582-09-8	Trifluralin
51-79-6	Urethane (monomer) (Ethyl ester carbamic acid)
7440-62-2	Vanadium (fume or dust)
108-05-4	Vinyl acetate

TABLE A.1
(CONTINUED)

CAS Number	Substance
593-60-2	Vinyl bromide
75-01-4	Vinyl chloride (monomer) (Chloroethane)
75-35-4	Vinylidine chloride (1,1-Dichloroethylene)
1330-20-7	Xylene (mixed isomers) (Dimethyl benzene)
108-38-3	m-Xylene (m-Dimethyl benzene)
95-47-6	o-Xylene (o-Dimethyl benzene)
106-42-3	p-Xylene (p-Dimethyl benzene)
7440-66-6	Zinc (fume or dust) (and compounds)

APPENDIX B

B.1 Method TO-1

Method TO-1 is suitable for the determination of certain nonpolar volatile organic compounds (VOC's) having boiling points in the range of 80° - 200° C. An ambient air sample is drawn through a cartridge containing Tenax^R. The analytical detection limit varies with the analyte. Detection limits of 1-200 pptv are achievable using a 20L sample.

Certain VOC's are trapped on the tenax while highly volatile organic compounds and most inorganic atmospheric constituents pass through the adsorbent. The cartridge is sealed and returned to the laboratory for thermal desorption and subsequent GC/MS analysis. Mass spectrometry is not necessarily required if it can be documented that satisfactory results can be obtained with an FID or ECD.

Contamination of the Tenax cartridge is a common problem with the method. Caution must be exercised during all operations to minimize contamination of the Tenax.

Breakthrough of analytes is another common problem. Backup cartridges must be used, and distributed air volume sampling techniques are recommended.

B.2 Method TO-2

Method TO-2 is suitable for the determination of certain nonpolar volatile organic compounds having boiling points in the range of -15° to 120° C. The analytical detection limit varies with the analyte. Detection limits of 0.01-1 ppbv are achievable using a 20L sample.

An ambient air sample is drawn through a cartridge containing a carbon molecular sieve adsorbent. Volatile organic compounds are retained by the adsorbent while major inorganic atmospheric constituents pass through. The cartridge is sealed and returned to the laboratory for analysis. Prior to analysis, the cartridge is purged with pure, dry air to remove adsorbed moisture. Following the dry air purge, the cartridge is heated and then purged with helium. Organic compounds are desorbed during this process and subsequently collected in a cryogenic trap. The collected organics are then flash evaporated into a capillary column GC/MS system for identification and quantification.

Contamination of the carbon molecular sieve is a common problem with the method. Caution must be exercised during all operations to minimize contamination of the adsorbent.

Breakthrough of analytes is another common problem. Backup cartridges must be used, and distributed air volume sampling techniques are recommended.

B.3 Method TO-3

Method TO-3 is suitable for the determination of certain highly volatile compounds having boiling points in the range of -10° to 200° C. The analytical detection limit varies widely with the analyte and the detector system. Detection limits in the low ppbv can be achieved with certain hydrocarbons, using an FID and a 20L sample. Lower detection limits are achievable with an ECD.

An ambient air sample is drawn through a collection trap submerged in either liquid oxygen or, preferably, liquid argon. The collection trap is plumbed to a gas chromatograph through a rotary, multi-port sampling valve. Following sample collection, the multi-port valve is switched so that carrier gas sweeps the contents of the trap onto the head of a cooled (-50°) GC column. Simultaneously, the liquid cryogen is removed, and the trap is heated to aid in the transfer of sample contents from the trap to the head of the GC column. The GC column is temperature programmed to yield the desired chromatographic separation. Compounds eluting from the column are then quantified using an FID or an ECD.

This method has two significant limitations. First, compounds having similar retention times will co-elute, making determination of a compound of interest difficult. This problem can be minimized by using selective detection systems and appropriate columns. Secondly, condensation of moisture can result in ice plugging of the trap or GC column. Permeation dryers have been used to reduce moisture problems; however, compounds of interest can be lost with permeation dryers, and permeation dryers can be a source of organic contaminants.

B.4 Method TO-4

Method TO-4 is suitable for the determination of a variety of organopesticides and polychlorinated biphenyls in ambient air. Because the high volume sampler operates at a very high flow rate (200-280 L/minute) and because the ECD is a highly sensitive detector, it is possible to detect very low ambient concentrations of PCB's and organopesticides, using this procedure. Detection limits of less than 1 ng/m^3 are achievable during a 24-hour sampling period.

An ambient air sample is collected with a modified high volume sampler consisting of a glass fiber filter with a polyurethane foam (PUF) backup adsorbent cartridge. The glass fiber filter and PUF cartridge are returned to the laboratory for analysis. The PCB's and pesticides are recovered by Soxhlet extraction, using 5% ether in hexane. The extracts are concentrated by Kuderna-Danish techniques and cleaned up using column chromatography. The resulting extracts are then analyzed for pesticides and PCB's, using gas chromatography with electron capture detection in accordance with U.S. EPA Method 608.

Organochlorine pesticides and PCB's are complex mixtures of individual compounds, and it can be very difficult to quantify a specific constituent of a multicomponent mixture. Contamination of glassware and sampling equipment is a common problem, and care should be taken to minimize contamination during equipment cleaning and handling .

B.5 Method TO-5

Method TO-5 is suitable for the determination of certain individual aldehydes and ketones in ambient air. With proper attention to reagent purity, the method can detect most monofunctional aldehydes and ketones at the 1-2 ppbv level.

Ambient air is drawn through a midget impinger containing 10 ml of 0.05% 2,4 - dinitrophenylhydrazine (DNPH) in 2N Hcl and 10 mL of isooctane. Aldehydes and ketones react with the DNPH to form stable 2,4 - dinitrophenylhydrazones (DNPH derivatives). The impinger contents are transferred to a screw cap vial and returned to the laboratory. The isooctane layer is removed, and the aqueous layer is extracted with hexane/methylene chloride. The extract is then recombined with the previously removed isooctane and evaporated to dryness under a stream of nitrogen. The residue is dissolved in methanol and analyzed using reversed phase HPLC with an ultraviolet absorbance detector operating at 370 nm.

Isomeric aldehydes and ketones may be unresolved by the HPLC system and may cause quantification and identification problems. Careful attention should therefore be given to selection of the separation column and mobile phase. Formaldehyde and acetone contamination of the DPNH reagent are common problems. Acetone contamination is unavoidable, and the method is not suitable to the determination of acetone. Formaldehyde contamination problems can be minimized by using fresh reagents (<48 hours old) and storing the DNPH reagent in an uncontaminated environment.

B.6 Method TO-6

Method TO-6 is suitable for the determination of phosgene in ambient air. The analytical detection limit is approximately 0.1 ppbv.

Ambient air is drawn through a midget impinger containing 10 ml of 2/98 aniline/toluene (v/v). the phosgene reacts with aniline to form 1,3 - diphenylurea. The impinger contents are transferred to a screw-cap vial and returned to the laboratory for analysis. The vial is placed on a heater block, and the liquid is evaporated under a stream of nitrogen. The residue is dissolved in acetonitrite, and the 1,3 - diphenylurea is analyzed using reverse-phase HPLC with a UV absorbance detector operating at 254 nm.

There are few interferences with this method. Chloroformates can react with aniline to form urea which coelutes with the 1,3 - diphenylurea and is detectable by UV. Reagent purity is an important consideration because traces of 1,3 - diphenylurea have been found in reagent grade aniline.

B.7 Method TO-7

Method TO-7 is suitable for the analysis of N-nitrosodimethylamine in ambient air. Analytical detection limits of lug/m^3 are achievable using GC/MS.

Ambient air is drawn through a cartridge containing Thermosorb/N adsorbent. The cartridges are returned to the laboratory and pre-eluted with 5 mL of dichloromethane (in same direction as sample flow). Residual dichloromethane is removed by purging the cartridge with air in the direction of sample flow. The cartridges are then eluted in reverse direction with 2 mL of acetone. The N-nitrosodimethylamine is then determined by GC/MS.

Breakthrough of N-nitrosodimethylamine is apparently not a problem with flow rates of approximately 2L/minute and sample volumes of 300L. Compounds having similar retention times and yielding detectable m/e 74 ion fragments may interfere with the method. These problems are minimized by the pre-elution step.

B.8 Method TO-8

Method TO-8 is suitable for the analysis of phenol and cresols (methylphenols) in ambient air. Analytical detection limits of 1-5 ppbv are readily achievable.

Ambient air is drawn through a series of two midget impingers, each containing 15 mL of 0.1 N NaOH. The phenols and methylphenols are trapped as phenolates. The impinger contents are transferred to a screw cap vial and returned to the laboratory for analysis. The solution is cooled in an ice bath and adjusted to a pH of less than 4 by the addition of 1 ml 5% H_2SO_4 (v/v). The sample volume is adjusted to 25 mL with distilled water, and an aliquot is removed for analysis by reverse-phase HPLC. Electrochemical detection, fluorescence detection, or ultraviolet detection (254 nm) can be used, depending on sample cleanliness.

Compounds that co-elute with compounds of interest will interfere with the method. Column and mobile phase selection are, therefore, important considerations. Phenolic compounds of interest may be oxidized during sampling; consequently, appropriate validation experiments are in order.

B.9 Method TO-9

Method To-9 is suitable for the delamination of a variety of polychlorinated dibenzo-p-dioxins (PCDD's) in ambient air. Detection limits below 15 pg/m^3 are readily achievable.

Ambient air is drawn through a glass fiber filter and a polyurethane foam (PUF) adsorbent cartridge by means of a high volume sampler. Following sample collection, the filter and the PUF cartridge are removed and returned to the laboratory for analysis. The filter and PUF cartridge are extracted using benzene. The extract is concentrated using Kuderna-Danish technique, diluted with hexane, and cleaned up using column chromatography. The cleaned extract is then analyzed by high resolution gas chromatography/high resolution mass spectrometry.

This method is very complicated and subject to a variety of interferences. Chemicals that co-elute with compounds of interest and produce similar m/e ratios will interfere with quantification and identification. Reagent purity and glassware cleanliness are of utmost importance because of the very low levels of PCDD's that are being analyzed.

B.10 Method TO-10

Method TO-10 is suitable for the determination of a variety of organopesticides in ambient air. The analytical detection limit varies with the analyte, sample volume, and detector used.

An ambient air sample is drawn through a polyurethane foam (PUF) sorbent cartridge at one to five L/minute. The PUF cartridge is returned to the laboratory for recovery of the pesticides by Soxhlet extraction with five percent diethyl ether in hexane. The extract is concentrated using Kuderna-Danish techniques and cleaned up using column chromatography techniques. The resulting extract is then analyzed for pesticides, using gas chromatography with electron capture detection. HPLC with UV detection may be preferable for certain pesticides.

Organochlorine pesticides are complex mixtures of individual compounds, and it can be difficult to quantify a specific constituent of a multicomponent mixture. As with any chromatographic technique, co-elution of interferents can be a problem.

B.11 Method TO-11

Method TO-11 is suitable for the determination of formaldehyde in ambient air. This method can be used for either long- or short-term sampling periods. The analytical detection limit varies with sample volume; detection limits in the one to 20 ppb range are achievable with sample volumes of approximately 750 liters.

An ambient air sample is drawn through a user-prepared cartridge containing 2,4-dintrophenylhydrazine (DNPH)-coated silica gel at a flow rate of 500-1200 mL/minute. The cartridges are returned to the laboratory in screw-cap glass vials. The cartridges are then removed from the vials and washed with acetonitrile by gravity feed elution. The eluate is diluted volumetrically and an aliquot is removed for determination of the DNPH-formaldehyde derivative by isocratic reverse phase HPLC with UV detection at 350 nm.

Formaldehyde contamination of the DNPH reagent is common and will obscure results if appropriate blank determinations are not made. As with any chromatographic procedure, co-elution of interferents can be a problem.

B.12 Method TO-12

Method TO-12 is suitable for the determination of a variety of non-methane organic compounds (NMOC) in ambient air. Detection limits in the low PPB's are achievable for many compounds.

This method permits the use of two sampling procedures: A whole air sample is either extracted directly from the ambient air and analyzed on site by the GC system or collected into an evacuated sample canister and analyzed off site.

A fixed-volume portion of the sample air is drawn through a glass-bead filled trap cooled with liquid argon to approximately -186°C. The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured but must be precisely repeatable between the calibration and the analytical phases. After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID base line restabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C to revolatize the NMOC's. The revolatized NMOC's are flushed from the trap via carrier gas flow and discharged onto the chromatographic column where separation occurs.

B.13 Method TO-13

Method TO-13 is suitable for the analysis of polynuclear aromatic hydrocarbons in ambient air, using either GC or HPLC. At the time of the TAD publication, Method TO-13 had not been formally published.

B.14 Method TO-14

Method TO-14 is suitable for the analysis in ambient air of VOC's and SVOC's which have been tested and determined to be stable when stored in pressurized and subatmospheric canisters. The detection limit varies with the analyte, but PPB levels are readily achievable.

Both subatmospheric and pressurized sampling modes use an initially evacuated canister and a sample line purge vacuum pump for sample collection. Pressurized sampling requires an additional pump (metal bellows type) to provide positive pressure in the sample canister. A sample of ambient air is drawn into a sampling train comprised of an initially evacuated canister and various components that regulate the rate and duration of sampling and provide sample integrity.

After the air sample is collected, the canister valve is closed: an identification tag is attached to the canister, and the canister is then shipped to a predetermined laboratory for analysis. Upon receipt at the laboratory, the canister tag data are recorded in a dedicated logbook, and the canister is attached in-line to the analytical system.

In preparation for analysis, the VOC's are concentrated by condensation in a cryogenic trap. The cryogen is removed, and the temperature of the trap is raised. The VOC's originally collected in the trap are revolatilized and carried to the GC column for VOC speciation followed by multi-detector quantitation.

Each sample is analyzed by the following instrumentation and procedures:

1. gas chromatography-flame ionization detector and electron capture detector (GC-FID-ECD)

2. gas chromatography-mass selective detector-scan (GC-MSD-SCAN)

3. gas chromatography-mass selective detector-selected ion monitoring (GC-MSD-SIM)

Preliminary identification of VOC species in the sample (including any polar compounds present) is provided by the FID and ECD analyses. Positive identification of VOC species is provided by the gas chromatograph in the SCAN mode. Polar compounds are not identified by the MSD-SCAN analyses, because a Nafion tube dryer is used to remove water from the sample, prior to MSD analysis. Preliminary quantitation of the targeted VOC's is performed by the MSD-SIM analyses.

APPENDIX C
GLOSSARY

Absorbance: The logarithm to the base of 10 of the reciprocal of transmittance.

Accuracy: The degree to which a measured value agrees with the true or accepted reference value (e.g. pollutant concentration), usually expressed as the percentage of the true or reference value represented by the difference between the two (true and measured) values.

Acidic compound: A compound which dissociates in water to form a hydrogenion (proton) and the corresponding anion (for example, acetic acid dissociates into a hydrogen ion and the acetate anion).

Adsorbate: Material that has been retained by the process of adsorption.

Adsorbent: Solid material on the surface of which adsorption takes place.

Adsorption: A physical process in which molecules of gas, of dissolved substances, or of liquids adhere in an extremely thin layer to the surfaces of solid bodies with which they are in contact.

Aerosol: A dispersion of solid or liquid particles in gaseous media.

Air at normal conditions (standard air): Air at 50 percent relative humidity, 70°F and 29.92 in. Hg (21°C and 760 mm Hg). These conditions are chosen in recognition of the data which have been accumulated on air-handling equipment. They are sufficiently near the 25°C and 760mm Hg commonly used for indoor air contamination work that no conversion or correction ordinarily need be applied.

Air pollution: The presence of unwanted material in the air. The term "unwanted material" here refers to material in sufficient concentrations, present for a sufficient time, and under circumstances to interfere significantly with comfort, health, or welfare of persons or with the full use and enjoyment of property.

Aliquot: A representative portion of the whole.

Alkali flame detector (AFD): See nitrogen phosphorus detector.

Atmosphere, an: A unit of pressure equal to the pressure exerted by a vertical column of mercury 760 mm high, at a temperature of 0°C, and under standard gravity.

Atmosphere, synthetic: A specific gaseous mass containing any number of constituents and in any proportion produced by man for a special purpose.

Atmosphere, the: The whole mass of air surrounding the earth and composed largely of oxygen and nitrogen.

Basic compounds: Compounds which protonate (add a hydrogen ion) in water to form a cation (e.g. amines).

Breathing zone: That location in the atmosphere at which persons breathe.

Bubbler: A sampling device consisting of a gas disperser immersed in an absorbing liquid.

Bubbler, fritted: A bubbler having a frit as the gas disperser.

Calibration: Establishment of a relationship between the responses of a measurement system obtained by introducing various calibration standards into the system. The calibration levels should bracket the range of levels for which actual measurements are to be made.

Chemiluminescence detection: The measurement of emitted visible or ultraviolet radiation resulting from the reaction of a pollutant with a reactive gas (for example, detection of nitric oxide by reaction with ozone).

Column chromatography: A separation technique wherein the stationary phase is a solid (e.g. silica gel) and the mobile phase is a liquid, usually an organic solvent or mixture of solvents. The technique is usually performed using a tubular column operating an ambient pressure and is most commonly used for the removal of potential interferences, prior to determination of the compound of interest.

Collection efficiency: The percentage of a specified substance retained by a gas cleaning or sampling device.

Colorimeter: An instrument used for color measurement based on optical comparison with standard colors.

Condensate: Liquid or solid matter formed by condensation from the vapor phase. In sampling, the term is applied to the components of an atmosphere which have been isolated by simple cooling.

Condensation: The process of converting a material in the gaseous phase to a liquid or solid state by decreasing temperature, by increasing pressure, or both. Usually in air sampling, only cooling is used.

Contaminant: A material added by human or natural activities which may, in sufficient concentrations, render the atmosphere unacceptable.

Cryogenic collection (trapping): A sampling process wherein an air sample is passed through a cooled trap (usually using liquid argon or material similar to the cryogen) to collect organic compounds.

Density: The mass per unit volume of substance.

Derivatization: A sampling and analysis process wherein a compound to be monitored is converted to another more stable and/or readily detectable compound via chemical reaction during the sampling or analysis step.

Desorption: The process of freeing from a sorbed state.

Detection limit: The minimum quantity of a compound which yields a "measureable response." Many statistical definitions of "measureable response" are in use. One must be careful to differentiate "instrumental detection limit," which refers to the minimum quantity of detectable material introducible into a measurement system from "method detection limit" which refers to the minimum concentration of compound in the sample which, when carried through the entire sampling and analysis process, can be detected.

Diffusion, molecular: A process of spontaneous intermixing of different substances, attributable to molecular motion and tending to produce uniformity of concentration.

Dispersion: The most general term for a system consisting of particulate matter suspended in air or other gases.

Diurnal: Recurring daily. Applied to air contaminants, diurnal indicates variations (in concentration) that follow a distinctive pattern and which recur from day to day.

Droplet: A small liquid particle of such size and density as to fall under still conditions but which may remain suspended under turbulent conditions.

Dust: A term loosely applied to solid particles predominantly larger than colloidal and capable of temporary suspension in air or other gases. Dusts do not tend to flocculate except under electrostatic forces; they do not diffuse but settle under the influence of gravity. Derivation from larger masses through the application of physical force is usually implied.

Efficiency: A measure of the performance of a collector. Usually it is the ratio of the amount collected to the inlet loading, expressed in percentage.

Efficiency, fractional: The mean collection efficiency for specific size fractions of a contaminant. Commonly this term has been applied to the performance of air cleaning equipment toward particulate matter in various size ranges.

Electron capture detector (ECD): A detection device for gas chromatography which responds sensitively and selectively to electron deficient (e.g. halogenated, nitrosubstituted) compounds.

Elute: To remove sorbed materials from a sorbent by means of fluid.

Emissions: The total of substances discharged into the air from a stack, vent, or other discrete source.

Filter: A porous medium for collecting particulate matter.

Filter, controlled pore: A filter of various plastics or metals having a structure of controlled uniform pore size. Sometimes referred to as a membrane or molecular filter.

Flame ionization detector (FID): A detection device for gas chromatography which responds to most organic compounds.

Flame photometric detector (FPD): A detection device for gas chromatography which responds selectively to sulfur- and phosphorous-containing compounds.

Flowmeter: An instrument for measuring the rate of flow of a fluid moving through a pipe or duct system. The instrument is calibrated to give either volume or mass rate of flow.

Fluorescence spectrometery: The measure of ultraviolet or visible radiation emitted by a compound after excitation with radiation of a lower wavelength. The technique is widely used for the determination of polynuclear aromatic hydrocarbons.

Fly ash: The finely divided particles of ash entrained in flue gases arising from the combustion of fuel. The particles of ash may contain incompletely burned fuel. The term has been applied predominantly to the gas-born ash from a boiler with a spreader stoker, an underfeed stoker, and pulverized fuel (coal) firing.

Fog: A term loosely applied to visible aerosols in which the dispersed phase is liquid. Formation by condensation is usually implied. In meteorology, a dispersion of water or ice.

Fractionation: The process of separating a mixture into components having different properties (as by distillation, precipitation, or screening).

Freezing out: See sampling, condensation, or cryogenic collection.

Frit: A porous material permeable to gas flow usually made by sintering microbeads of an appropriate material.

Fume: Properly, the solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometime coalesce. Popularly, the term is used in reference to any or all types of contaminant and, in many laws or regulations, with the added qualification that the contaminant have some unwanted action.

Gas: One of the three states of aggregation of matter, having neither independent shape nor volume and tending to expand indefinitely.

Gas chromatography (GC): A separation technique for organic compounds wherein the stationary phase is a solid, liquid coated on a solid, or liquid coated or bonded to the interior column wall (capillary column) and the mobile phase is an inert gas.

Gas meter: An instrument for measuring the quantity of a gas passing through the meter.

Grab sample: See sampling, instantaneous.

Gustiness: Now referred to as intensity of turbulence, which is defined as the ratio of the root mean square of wind velocity fluctuations to the mean wind velocity.

Hall electrolytic conductivity detector (HECD): A detection device for gas chromatography which responds selectively to halogenated, sulfur containing compounds or to nitrogen containing compounds (depending on operating mode selected).

Halogenated compound: A compound containing chlorine, bromine, or iodine.

High performance liquid chromatography (HPLC): A separation technique wherein the mobile phase is a liquid and the stationary phase is a solid, usually having a particle diameter of 10 um or less. HPLC is similar to column chromatography, except that small particle diameter stationary phases and high pressures are used to achieve faster analysis and greater resolution.

Impaction: A forcible contact of particles of matter; a term often used synonymously with impingement.

Impactor: A sampling device that employs the principle of impaction (impingement). The "cascade impactor" refers to a specific instrument which employs several impactions serially to collect successively smaller sizes of particles.

Impingement: The act of bringing matter forcibly into contact. As used in air sampling, impingement refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface.

Impinger: See bubbler.

Internal standard: A known quantity of a reference compound added to a collected sample for use in the quantification of other compounds.

Inversion: A reversal of the normal atmospheric temperature gradient, thus an increase of air temperature with increasing altitude.

Ionic or ionizable compound: A compound which dissociates in water to give ionic species (i.e. acidic or basic compounds).

Isokinetic: A term describing a condition of sampling, in which the flow of gas into the sampling device (at the opening or face of the inlet) has the same flow rate and direction as the ambient atmosphere being sampled.

Lapse rate: The rate of change of the absolute value of any meteorological element with increase of height. (When used without a modifier, it refers to the rate of decrease of temperature with increase of height).

Mass concentration: Concentration expressed in terms of mass of substance per unit volume of gas or liquid.

Mass spectroscopy: A widely used analytical technique capable of identifying and quantifying organic materials on the basis of the mass fragmentation pattern. Most commonly used for organic analysis in combination with gas chromatography (i.e. GC-MS).

Mass median size: A measurement of particle size for samples of particulate matter, consisting of that diameter at which the mass of all larger particles is equal to the mass of all smaller particles.

Meteorology: The science dealing with the atmosphere and weather conditions.

Micro-climatology: The science that deals with the climate of restricted areas and investigates their phenomena and causes.

Micro-meteorology: The study of the meteorological characteristics of a local site that is usually small and often confined to a shallow layer of air next to the ground.

Mist: Liquid, usually water in the form of particles suspended in the atmosphere at or near the surface of the earth; small water droplets floating or falling, approaching the form of rain, and sometimes distinguished from fog as being more transparent or as having particles perceptibly moving downward.

Mobile phase: In chromatography, the separation medium which is in motion.

Month: A base of 30 days to which reported results of outdoor analyses are calculated.

Neutral compound: A compound which does not ionize in water (e.g. not acidic or basic).

Nitrogen-phosphorous detector (NPD): A detection device for gas chromatography which is sensitive and selective for nitrogen- and phosphorous-containing organic compounds.

Opacity rating: A measurement of the opacity of emissions, defined as the apparent obscuration of an observer's vision to a degree equal to the apparent obscuration of smoke of a given rating on the Ringelmann Chart.

Orifice meter: A flowmeter employing as the measure of flow rate the difference between the pressures measured on the upstream and downstream sides of the orifice (that is, the pressure differential across the orifice) in the conveying pipe or duct.

Particle: A small discrete mass of solid or liquid matter.

Particle concentrations: Concentration expressed in terms of number of particles per unit volume of air or other gas. NOTE: On expressing particle concentration the method of determining the concentration should be stated.

Particle fall: A measurement of air contamination consisting of the mass rate at which solid particles deposit from the atmosphere. A term used in the same sense as the older terms "dust fall" and "soot fall" but without any amplication as to nature and source of the particles.

Particle size: An expression for the size of liquid or solid particles expressed as the average or equivalent diameter.

Particle size distribution: The relative percentage by weight or number of each of the different size fractions of particulate matter.

Particulate: Solids or liquids existing in the form of separate particles.

Phase distribution: The relative amounts of a compound associated with the particle and gas phases in the atmosphere.

Photochemical reaction: Any chemical reaction initiated as a result of absorption of light.

Photochemical smog: A type of air pollution resulting from photochemical reactions.

Photoionization detector (PID): A detection device for gas chromatography which detects aromatic, halogenated, and olefinic compounds but is relatively insensitive to aliphatic compounds. The selectivity can be adjusted by the choice of lamp energy.

ppb: A unit of measure of the concentration of gases in air expressed as parts of the gas per billion (10^9) parts of the air-gas mixture, normally both by volume (ppbv).

ppm: A unit of measure of the concentration of gases in air expressed as parts of the gas per million parts of the air-gas mixture, normally both by volume (ppmv).

Precipitation, electrostatic: A process consisting of the separation of particulate matter from air or other gases under the influence of an electrostatic field.

Precipitation, meteorological: The deposit on the earth of water from the atmosphere in the form of hail, mist, rain, sleet, and snow. Deposits of dew, fog, and frost are excluded.

Precipitation, thermal: A process consisting of the separation of particulate matter from air and other gases under the influence of a relatively large temperature gradient extending over a short distance. In the "Thermal Precipitator" (a sampling instrument), the air or gas is drawn slowly through a narrow chamber across which extends a heated wire, particulate matter being deposited upon the adjacent collecting surface.

Precipitation, ultrasonic: A process consisting of the separation of particulate matter from air and other gases following agglomeration induced by an ultrasonic field.

Precipitator, electrostatic: Apparatus employing electrostatic precipitation for the separation of particles from a gas stream. The apparatus may be designed either for sampling or for cleaning large volumes of gas.

Precision: The degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the mean result obtained by repetitive testing of a homogeneous sample under specified conditions. The precision of a method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations.

Pressure, gage: The difference between pressure existing within a system and that of the atmosphere. Zero gage pressure is equal to atmospheric pressure.

Pressure, static: The pressure of a fluid at rest or in motion, exerted perpendicularly to the direction of flow.

Pressure, total: The pressure representing the sum of static pressure and velocity pressure at the point of measurement.

Pressure, velocity: That pressure caused by and related to the velocity of the flow of fluid; a measure of the kinetic energy of the fluid.

Probe: A tube used for sampling or for measuring pressures at a distance from the actual collection or measuring apparatus. It is commonly used for reaching inside stacks and ducts.

Quality assurance: A system of activities designed to provide assurance that the quality control system is performing adequately.

Quality control: A system of specific efforts designed to test and control the quality of the data obtained.

Radiosonde: A miniature radio transmitter with instruments that is carried aloft (as by an unmanned balloon) for broadcasting every few seconds by means of precise tone signals or other suitable method the humidity, temperature, pressure, or other parameter.

Resin: A porous polymer adsorbent such as Tenax^{R} for collection of gas phase organic compounds.

Rotometer: A device, based on the principle of Stoke's law, for measuring rate of fluid flow. It consists of a tapered vertical tube having a circular cross section and containing a float that is free to move in a vertical path to a height dependent upon the rate of fluid flow upward through the tube.

Sample, cumulative: A sample obtained over a period of time (1) with the collected atmosphere being retained in a single vessel or (2) with a separated component accumulating into a single whole. Examples are dust sampling, in which all the dust separated from the air is accumulated in one mass of fluid; the absorption of acid gas in an alkaline solution; and collection of air in a plastic bag or gasometer. Such a sample does not reflect variations of concentration during the sampling period.

Sample, running: Withdrawal of a portion of the atmosphere over a period of time along with continuous analysis or with separation of the desired material continuously and in a "linear" form. Examples are continuous withdrawal of the atmosphere accompanied by absorption of a component in a flowing stream of absorbent or by filtration in a moving strip of paper. Such a sample may be obtained with a considerable concentration of the contaminant, but it still indicates fluctuations in concentration which occur during the sampling period.

Sampling: A process consisting of the withdrawal or isolation of a fractional part of a whole. In air or gas analysis, the separation of a portion of an ambient atmosphere with or without the simultaneous isolation of selected components.

Sampling, condensation: A process consisting of the collection of one or several components of a gaseous mixture by simple cooling of the gas stream in a device which retains the condensate.

Sampling, continuous: Sampling without interruptions throughout an operation or for a predetermined time.

Sampling,. instantaneous: Obtaining a sample of an atmosphere in a very short period of time, so that this sampling time is insignificant in comparison with the duration of the operation or the period being studied.

Sampling, intermittent: Sampling successively for limited periods of time throughout an operation or for a predetermined period of time. The duration of sampling periods and of the intervals between are not necessarily regular and are not specified.

Sampling, source: Withdrawal, with or without simultaneous isolation of specific components, of a portion of the offgases from a source of pollutants. Sometimes referred to as stack sampling when withdrawal is from a chimney, duct, or stack.

Sampling train: The assemblage of equipment necessary to sample atmospheres.

Scrubber: A type of apparatus used in sampling and in gas cleaning, whereby the gas is passed through a space containing wetted "packing" or spray.

Sensor: A device designed to respond to a physical stimulus (as temperature, illumination, and motion) and to transmit a resulting signal for interpretation or measurement or for operating a control.

Series collection: An operation involving the use of two or more collectors joined in series.

Settling velocity: The terminal rate of fall of a particle through a fluid, as induced by gravity or other external force; the rate at which frictional drag balances the accelerating force (or the external force).

Smog: A term derived from the terms "smoke" and "fog", applied to extensive atmospheric contamination by aerosols, these aerosols arising partly through natural processes and partly from the activities of human subjects. Now sometimes used loosely for any contamination of the air.

Smoke: Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material, and present in sufficient quantity to be observable independently of the presence of other solids.

Soot: Agglomerations of particles of carbon impregnated with "tar", formed in the incomplete combustion of carbonaceous material.

Sorbent: A liquid or solid medium in or upon which materials are retained by absorption or adsorption.

Soxhlet apparatus: An apparatus for use in extracting fatty or other material with a volatile solvent (as ether, alcohol, or benzene) in which the solvent is recirculated by evaporation and subsequent condensation.

Specific gravity: The ratio of the density of the substance in question to the density of a reference substance at specified conditions of temperature and pressure.

Spectrometry: A method of identification of a compound by identification of the spectrum produced.

Spectrophotometry; A method for identification of substances and determination of their concentrations by measuring light transmittance in different parts of the spectrum.

Standard operating procedure (SOP): A detailed description of the operation of a sampling or analysis system for a specific application.

Stationary phase: In chromatography, the separation medium which has held fixed.

Temperature, absolute: (a) Temperature measured on the thermodynamic scale, designated as Kelvin (K). (b) Temperature measured from absolute zero (-273.18°C or -459.58°F). The numerical values are the same for both the Kelvin scale and the ideal gas scale.

Tenax^R: A polyphenyloxide polymer prepared as a porous adsorbent for determination of gas phase organic compounds. The relatively good thermal stability of Tenax^R allows recovery of adsorbed organics by thermal desorption.

Thermionic detector: See nitrogen-phosphorus detector.

Thin layer chromatography (TLC): A chromatographic technique wherein the stationary phase is a solid coated in a thin layer on a glass plate and the mobile phase is a liquid. The technique is commonly used for the determination of polynuclear aromatic hydrocarbons, using fluorescence detection.

Validation, data: A systematic effort to review data to identify outliers or errors and thereby cause deletion or flagging of suspect values to assure the validity of the data for the user.

Validation, method: The process of documenting the performance characteristics of a method through the analysis of blanks and replicate samples of known analyte concentration. The analyte concentrations tested should cover the range likely to be encountered in the actual monitoring situation.

Vapor: The gaseous phase of matter that normally exists in a liquid or solid state.

Volume concentration: Concentration expressed in terms of gaseous volume of substance per unit of air or other gas usually expressed in parts per million (ppmv) or parts per billion (ppbv).

Year: A period of 12 30-day months, at the end of which results of analyses of outdoor air are reported.

APPENDIX D
EQUIPMENT/INSTRUMENT VENDORS

VENDOR	PRODUCT
Ace Glass, Inc. 1430 N. West Blvd. Vineland, NJ 08360	Sampling Train Glassware
Air Products & Chemicals, Inc. P.O. Box 538 Allentown, PA 18105	Specialty Gases
Alltech Associates 2051 Waukegan Rd. Deerfield, IL 60015	Chromatography supplies and standards
Alnor Instrument Co. 7555 N. Linder Ave. Skokie, IL 60077	Wind Velocity/Direction Instrumentation
Alphagaz Specialty Gases Div. of Liquid Air Corp. 2121 N. California Blvd. Walnut Creek, CA 94596	Specialty Gases
American Gas & Chemical Co., Ltd. 220 Pegasus Ave. Northvale, NJ 07647	Specialty Gases
Analabs Div. Foxboro Co. 80 Republic Drive North Haven, CT 06473	Chromatography supplies and standards
Analytical Instrument Development, Inc. Rt. 41 and Newark Rd. Avondale, PA 19311	Portable GC System
Andersen Samplers, Inc. 4215-C Wendell Dr. Atlanta, GA 30336	Canister Based Sampling System
The Anspec Co., Inc. P.O. Box 7730 Ann Arbor, MI 48107	Sampling Bags

VENDOR	PRODUCT
Brailsford and Co., Inc. 670 Milton Rd. Rye, NY 10580	Air sampling pumps
Brooks Instrument Div. 407 W. Vine Street Hatfield, PA 19440	Flow measuring and control devices
Bruker Instruments, Inc. Manning Park Billerica, MA 01821	Mobile mass Spectrometer System
Calibrated Instruments, Inc. 731 Saw Mill River Rd. Ardsley, NY 10502	Sampling Bags
California Measurements, Inc. 150 E. Montecito Ave. Sierra Madre, CA 91024	Particle Sizing Equipment
CEA Instruments, Inc. 16 Chestnut St. Emerson, NJ 07630	Colorimetric Analyzers
Chemical Data Systems 7000 Limestone Rd. Oxford, PA 19363	Data Management Systems
Chrompack, Inc. 1130 Rd. 202 Raritan, NJ 08869	GC Packing Material
Chrompack International B.V. Kuipersweg 6 P.O. Box 8033 Middleburg, The Netherlands 4330EA	GC Packing Material
Climatronics 104 Wilbur Pl. Bohemia, NY 11716	Meteorological Equipment

VENDOR	PRODUCT
Columbia Scientific Industries Corp. P.O. Box 203190 11950 Jollyville Rd. Austin, TX 78720	Thermal Desorption Equipment
Dasibi Environmental 515 W. Colorado St. Glendale, CA 91204	Gas dilution systems
Dionex Corp. 1228 Titan Way Sunnyvale, CA 94086	Ion Chromatographs
Dosimeter Corp. 11286 Grooms Rd. Cincinnati, OH 45242	Passive Monitors
E. I. DuPont de Nemours & Co., Inc. 1007 Market St. Wilmington, DE 19898	Passive Monitors
The Foxboro Company Foxboro, MA 02035	Infrared Spectrometer
General Metal Works Div. of Andersen Samplers 145 South Miami Ave. Village of Cleves, OH 45002	PUF and Hi Vol samplers
Gilian Instrument Corp. 8 Dawes Highway Wayne, NJ 07470	Sampling pumps
Hewlett-Packard Co. Mail Stop 2083 3000 Hanover St. Palo Alto, CA 94304	Analytical Instrumentation
HNU Systems, Inc. 160 Charlemont St. Newton, MA 02161	GC Systems and Photoionization Detectors

VENDOR	PRODUCT
The Lee Company P.O. Box 424 Westbrook, CT 06498	Teflon solenoid valves and components
Mace Corporation 2413 Lee Avenue S. El Monte, CA	Fabricated Teflon components
Matheson Gas Products 30 Seaview Dr. Secaucus, NJ 07094	Specialty Gases
Micro-Sensor 41762 Christy St. Freemont, CA 94538	GC Detection Systems
Millipore Corp. Ashby Rd. Bedford, MA 01730	Filter Media
Mine Safety Appliances Co. P.O. Box 426 Pittsburgh, PA 15230	Gas Sampling Tubes
MKS Instruments, Inc. 34 Third Avenue Burlington, MA 01803	Mass flow controllers
Monitor Labs, Inc. 10180 Scripps Ranch Blvd. San Diego, CA 92131	Detector Systems
National Draeger, Inc. P.O. Box 120 101 Technology Dr. Pittsburgh, PA 15230	Gas Sampling Tubes
Nutech 2806 Cheek Rd. Durham, NC 27704	Thermal desorbers and cryotrap

VENDOR	PRODUCT
Olympic Products Co. Div. Cone Mills 4100 Pleasant Garden Rd. Greensboro, NC 27406	Polyether foam for PUF sampling
Perkin-Elmer Corp. 761 Main Ave. Norwalk, CT 06859-0001	Analytical Instrumentation
Perma Pure Products, Inc. 8 Executive Drive Toms River, NJ 08754	Permeation dryer used with cryotrap
Porter Instrument Co. P.O. Box 326 Township Line Rd. Hatfield, PA 19440	Flow measuring devices
Scientific Glass & Instruments, Inc. P.O. Box 6 Houston, TX 77001	Scientific Glassware
Scientific Instrument Specialists 815 Courtney St. Moscow, ID 83843	Canister smapling systems
SCIEX Div. of MDS Health Group, Ltd. 55 Glen Cameron Rd. Thornhill, Ontario, Canada L3T 1P2	Mobile MS Services
Scott Specialty Gases 6141 Easton Rd. Plumsteadville, PA 18949	Specialty Gases
Sensidyne, Inc. 12345 Starkey Rd. Suite E Largo, FL 33543	Gas Sampling Tubes
Sentex Sensing Technology, Inc. 553 Broad Avenue Ridgefield, NJ 07657	Gas chromatograph (May be suitable for ambient sampling with ECD detector.)

VENDOR	PRODUCT
SKC, Inc. 334 Valley View Rd. Eighty Four, PA 15330	Industrial hygiene sampling supplies
Spectrex Corporation 3594 Haven Avenue Redwood City, CA 94063	Air sampling pumps
Supelco, Inc. Supelco Park Bellefonte, PA 16823	Chromotography Supplies
Technical Heaters, Inc. 710 Jessie St. San Fernando, CA 91340	Heated Sample Lines
Tekmar Co. P.O. Box 371856 Cincinnati, OH 45222-1856	Thermal Desorption Equipment
Teledyne Hastings-Raydist P.O. Box 1275 Hampton, VA 23661	Mass flow meters
Thermedics, Inc. 470 Wildwood St. Woburn, MA 01888-1799	Permeation tubes and diffusion vials
Thermo Environmental Instruments 108 South Street Hopkinton, MA 01748	Acquired product line of Analytical Instrument Development, Inc. Portable GC's and survey type PID's
TSI, Inc. 500 Cardigan Rd. P.O. Box 64394 St. Paul, MN 55164	Real Time Particle Analysis Equipment
Tylan Corporation 359 Van Ness Way Torrance, CA 90501	Mass flow controllers

VENDOR	PRODUCT
Valco Instruments Co., Inc. P.O. Box 55603 Houston, TX 77255	GC Sampling Valves
Varian Instrument Group 220 Humboldt Ct. Sunnyvale, CA 94089	GC Systems
Vici Metronics 2991 Corvin Dr. Santa Clara, CA 95051	Permeation Devices and Dynamic Calibration Equipment
Weathermeasure Division Qualimetrics Inc. P.O. Box 41039 Sacramento, CA 95841	Meteorological Equipment
Wedding & Associates, Inc. P.O. Box 1756 Fort Collins, CO 80522	High volume PUF samplers, PM-10 etc.
Wheaton Scientific 1000 N. Tenth St. Millville, NJ 08332	Scientific Glassware
XonTech, Inc. 6862 Hayvenhurst Avenue Van Nuys, CA 91406	Air sampling equipment for adsorbent tube sampling

APPENDIX E

CALIBRATION GAS STANDARDS

Cylinder gas standards of selected hazardous organic compounds at the ppb level are available through the USEPA for use in auditing the performance ambient air and stationary source measurement systems. Calibration standard ranges are 5 ppb and up. Information can be obtained by contacting:

Robert L. Lampe
USEPA
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, NC 27711
Phone:
Commercial - 919/541-4531
FTS - 629-4531

Group I Compounds

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene

Group II Compounds

Trichloroethylene
1,2 - dichloroethane
1,2 - dibromoethane
Acetonitrile
Trichlorofluoromethane (Freon-11)
Dichlorodifluoromethane (Freon-12)
Bromomethane
Methyl ethyl ketone
1,1,1-trichloroethane

Group III Compounds

Vinylidene chloride
1,1,2 trichloro-1,2,2-trifluoro-ethene (Freon-113)
1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon-114)
Acetone
1-4 Dioxane
Toluene
Chlorobenzene

Group IV Compounds

Acrylonitrile
1,3-Butadiene
Ethylene oxide
Methylene Chloride
Propylene oxide
ortho-xylene

Group V Compounds

Carbon tetrachloride
Chloroform
Perchloroethylene
Vinyl chloride
Benzene
Trichloroethylene
1,2-dichloroethane
1,2-dibromoethane
Methylene chloride
Trichlorofluoromethane (Freon-11)
Bromomethane
Toluene
Chlorobenzene
1,3-Butadiene
ortho-xylene
Ethyl benzene
1,2-dichloropropane